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Development of Microwave Plasma Detoxification Process for Hazardous Wastes. Phase I

Lockheed Missiles and Space Co, Inc, Palo Alto, Calif

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16 ABSTRACT

The microwave process described in this report is a relatively new application of what has been termed the "fourth state of matter", or the "plasma state". It is the first practical application of a microwave discharge to the decomposition of chemical compounds in significant quantities. This report describes a recent, successful, R&D effort in which a former "grams-per-hour" system was scaled up to a 5 to 7 pounds-per-hour system, and then its performance was verified with several typical hazardous materials. The materials tested and detoxified were Malathion, methyl bromide, polychlorinated biphenyls, phenylmercuric acetate, and Kepone. Complete detoxification resulted.

Further benefits of the process are the competitive, reasonable costs of about $0.20 per pound of material processed, including all costs.

The process warrants further development, namely additional scale-up to pilot and field units. Presently, units up to 100 pounds per hour or so appear feasible to construct and be operable within two or three years.

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April 1977

DEVELOPMENT OF MICROWAVE PLASMA DETOXIFICATION PROCESS FOR HAZARDOUS WASTES

PHASE I

by

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This report describes a current and successful research and development program whereby low-temperature microwave plasmas have been utilized to detoxify efficiently and safely various hazardous pesticides and organic wastes. As a result of the attainment of project objectives, further scale-up to larger size and capacity are under way at the pilot level, to be followed by field verification, which is in the planning stages.

Francis T. Mayo
Director
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PREFACE

Toxic organic substances, such as chlorinated hydrocarbons, and many organophosphorus, organonitrogen, and organometallic compounds are components of pesticides which have been withdrawn from use, are obsolete, or are components of hazardous industrial wastes. These materials must be managed or disposed of safely and effectively. A primary responsibility of the U.S. Environmental Protection Agency's Solid and Hazardous Waste Research Division (SHWRD) has been to encourage and support research and development efforts in the area of hazardous waste disposal technology. For compounds of nominal toxicity, laudable achievements have been accomplished in the technology of thermal destruction, chemical detoxification, long-term encapsulation, and special landfill methods. However, with the exception of high-cost incinerator processing, little or no new technology has been developed for the disposal of highly toxic, refractory, or extremely persistent wastes. These materials are described in the 1974 EPA Report to Congress, Disposal of Hazardous Wastes, SW-115

The microwave plasma process described in this report is a relatively new application of what has been termed the "fourth state of matter", or the "plasma state". It is the first practical application of a microwave discharge to the decomposition of chemical compounds in significant quantities.

TECHNICAL ABSTRACT

The process of microwave decomposition of organic materials has been applied to the detoxification/destruction of hazardous organic pesticides and wastes. The investigation began with the LPARL (Lockheed Palo Alto Research Laboratory) laboratory-size plasma system. Reaction efficiencies and reaction product identities were obtained. The detoxification process was then expanded to a larger-scale, continuous system employing custom-designed, commercially available hardware.

A primary objective of the program was concerned with evaluation of the effectiveness of the expanded-scale system using hazardous organic compounds and wastes of current interest. The products were identified to determine whether the products were innocuous or toxic, and whether recovery of useful materials as by-products was feasible.

Test Detoxifications in LPARL Unit

The materials selected for study were passed through the LPARL laboratory-size reactor, which handles 1 to 5 g/hr quantities, to evaluate conversion efficiency and to determine product identities. Oxygen and argon as carrier gases in combination with the toxic materials were tested and evaluated.

Conversion efficiency was calculated by means of mass-balance determinations; and product identity by means of instrumental analysis, e.g., infrared and mass spectroscopy. The mechanisms of the detoxification processes were postulated. Materials tested were pure Malathion liquid, liquid PCB's, phenylmercuric acetate solution, and methyl bromide gas.

Expanded-Scale Plasma System

An expanded-volume microwave plasma system was assembled from custom-designed commercially available microwave hardware. The plasma reactor tubes were constructed from transparent quartz. Materials feed systems for pure liquids, slurries, and solutions were designed and built to operate at reduced pressures, and installed with proper controls for monitoring the addition rates. Traps and separation units were installed as needed for the decomposition products.

Test Detoxifications in Expanded-Scale System

Liquid, slurry and solution materials were processed in the plasma reactor to evaluate conversion efficiency, by-product recovery, and product

identity. The principal goal was to maximize throughput at greater than 99.9% conversion. Materials detoxified were pure Malathion liquid, liquid PCB's, phenylmercuric acetate solution, and Kepone in the form of a solid powder, an aqueous slurry, and a solvent solution. Metallic mercury was recovered as a by-product from the decomposition of phenylmercuric acetate pesticide. The Kepone and organomercurial pesticides were considered as "real-world" systems because of their commercial sources of manufacture, and the nature of their composition as mixed system pesticides. Throughput of the system was maximized at 450 to 3200 g/hr (1 to 7 lb/hr), a multiplication factor of approximately 500 times that of the laboratory-scale unit. Specific engineering tasks have therefore been outlined for the design and construction of pilot-scale equipment and components for further expansion of the system to 30 lb/hr, to be followed later by a 100 lb/hr version.

This report was submitted in fulfillment of Contract No. 68-03-2100 by the Lockheed Palo Alto Research Laboratory of Lockheed Missiles & Space Co., Inc., under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period April 1975 through May 1976.

EXECUTIVE SUMMARY

This report describes recent, successful, research and development efforts to utilize low-temperature microwave plasmas for the safe and efficient detoxification of various hazardous wastes which threaten man and his environment. Approximately 10 million tons of such wastes are generated yearly, and are made up in part of the following types of materials:

- Pesticides which have been withdrawn from use
- Obsolete or below-specification toxic materials which cannot otherwise be utilized
- Industrial wastes from process streams, chemicals, explosives, etc.

Perhaps 10 to 30 percent of these wastes will need special methods for disposal. Some may be incinerated, or disposed of by other means. However, those containing highly toxic compounds will require more sophisticated techniques for disposal.

The EPA Solid and Hazardous Waste Research Division was attracted to the microwave plasma process during its search for new and novel means for detoxification of hazardous and toxic waste streams. Previously, a Lockheed-built bench-scale device had won the attention and support of the U.S. Army Edgewood Arsenal for the detoxification of trace nerve gas simulants in contaminated air streams or interior building environments. Proof of Concept tests were conducted during 1970-1972, with considerable success. Subsequently, the EPA supported a laboratory study to test the efficacy of the technique, using liquids and solids instead of the diluted gases. This program included actual pesticides and toxic materials instead of simulants.

During the first year's effort, 1975-1976, the process was remarkably successful in detoxifying all of the materials submitted for testing. These materials included a typical organophosphorus pesticide (Malathion), a rodent poison (methyl bromide), two polychlorinated biphenyl liquids (PCB's), a mercury-containing fungicide (phenylmercuric acetate), and Kepone, the highly chlorinated pesticide of some notoriety.

Scale-up operations were also successful. Starting at from 1 to 5 grams per hour in the laboratory-size plasma unit, the first level of throughput expansion was maximized at 450 to 3200 g/hr (1 to 7 lb/hr) - a multiplication factor of approximately 500 times.

Further benefits of the process are competitive, reasonable costs of about $.20/lb; the use of steam as well as oxygen as a carrier gas; and the potential verified in one case, for resource recovery of valuable materials, such as metallic mercury, from the organomercurial pesticide, phenylmercuric acetate.

Prospects for additional applications include the detoxification of carcinogenic compounds used by the U.S. Navy in their colored smoke formulations, the recovery of metal values from arsenic, cadmium, and zinc organometallic pesticides, and the decomposition of vinylchloride solid wastes and related products. The process warrants further R&D effort, namely, additional scale-up to larger sizes and capacities that will be compatible with anticipated needs at the pilot- and field-verification levels. The disposal of a few hundred pounds per hour will be evaluated and developed as a safe, essentially simple, and economic process for materials of high toxicity. Field demonstration testing and construction of systems at national or regional disposal sites are long-term projected goals.

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The Project Officer for the Environmental Protection Agency was Mr. Donald A. Oberacker; Mr. Richard A. Carnes served as Technical Consultant.

SECTION I

INTRODUCTION

Although the microwave plasma detoxification of pesticides and hazardous organic wastes is a relatively new process, investigations in plasma chemistry began as early as 1875 (1). In 1968, the Lockheed Palo Alto Research Laboratory (LPARL) was the first to investigate the application of a microwave discharge to the decomposition of toxic substances.

A series of experiments was run in order to show feasibility for decomposing toxic gases by an electrical discharge (2). Nerve gas simulants from the U.S. Army Edgewood Arsenal were tested in the process during 1970 - 1972. Decompositions were achieved at near 100 percent levels in the laboratory-size microwave cavity. Although the decomposition efficiencies were high, the throughput levels were low - about 1 to 5 g/hr (3, 4). This was the result of the small size of the reactor, which, however, utilized the largest cavity commercially available at the time. When it was determined that large-volume microwave applicators for expanded-scale plasma formation could be obtained on a custom basis from microwave hardware suppliers (5), the EPA Solid and Hazardous Waste Research Division (SHWRD) approved a feasibility study to test the process on several pesticides and toxic wastes. In the following report are described the chemistry of the detoxification reactions, an initial scale-up of the microwave hardware, and an evaluation of the process in which up to 3200 g/hr (7 lb/hr) were successfully decomposed to harmless or easily disposable effluents.

SECTION II

MICROWAVE PLASMA CHARACTERISTICS & BASIC PROCESS DESCRIPTION

In the present context, the term "microwave plasma" denotes an ionized gas produced by microwave-induced electron reactions with neutral gas molecules. To a first approximation, the electrons, rather than thermal or radiative sources, are the major contributors of energy for promotion of the chemical reactions. The reactions are initiated by collisions between the reactant molecules and electrons in the plasma. Organic free radicals are generally considered as the primary intermediates in this process. The ionized gas, or plasma, is also derived from the carrier gas which serves to transport the molecules into the plasma zone.

When microwave frequencies of 100 to 10,000 MHZ are used to induce ionization, the field in the cavity oscillates so rapidly that the force on the electrons changes direction before the electrons can travel far; thus, the plasma is not swept out of the discharge region (6). Consequently, the electrons and ionized gas particles remain within the discharge, thereby contributing to the chemical reactions in the plasma.

Microwave plasmas show many favorable characteristics (7) when compared with arc or electrode plasmas. These include the following:

- Production of high ionization levels and molecular dissociation without excess heating of the contained gas
- Construction of reaction vessels which are simple, free from contamination and less subject to damage because of the absence of internal electrodes
- Production of little or no electrical interference
- Absence of high voltages which can be easily contacted by operating personnel, i.e. absence of shock hazards.

Microwave plasmas, rather than radio frequency (RF) plasmas (1 to 100 MHz), have been chosen because an RF discharge is difficult or impossible to develop in uniform cross-section (8). This difficulty is detailed for gas phase oxidation reactions in a recent publication by Brown and Bell (9). It appears that the ability of RF plasmas to interact fully with liquids and solids would therefore be severely compromised.

Since the plasma decomposition mechanism involves electronic rather than thermal energy, the microwave applicator power coupling equipment can be maintained at low temperatures, that is, barely hot to the touch. The materials of construction which are associated with furnace or incinerator devices will therefore be generally unnecessary, and maintenance and repair expenses should be low or nonexistent.

The microwave plasmas described in this report were first produced in a laboratory-size resonant cavity, and then in three commercially-built trough waveguide applicators. Data on power levels utilized, flow rates, conversion efficiencies, and other plasma characteristics are enumerated in the sections associated with the respective toxic materials. Process equipment, hardware, and procedures are described in the next section.

SECTION 3

EQUIPMENT AND OPERATING PROCEDURES

3.1 LABORATORY-SCALE PLASMA UNIT

During the initial stages of the program, the plasma process was evaluated on pesticide materials in the same apparatus (4) which was utilized for decomposing the original organophosphonate simulants. In this way, a valid transition would be possible when the materials were run in the larger size microwave system, which was then under construction.

The laboratory unit was effectively the same as used previously, with the exception that the feed techniques required modification for injection of liquids and solutions. A schematic line diagram is shown in Figure 1, and a photograph in Figure 2. A block diagram of the microwave plasma detoxification system is given in Figure 3. This diagram applies to the different size systems irrespective of the type of microwave applicator or power source that is used.

The microwave power source was a Varian PPS-2, 5A unit, which has an output frequency of 2450 MHz and develops up to 2.5 kW. A Microlite 287 microwave leakage detector (Crystal Mfg. Co., Oklahoma City, OK) was used to monitor power leakage. Levels of leakage greater than 1 to 5 mW/cm^2, which is the lower limit of sensitivity of the apparatus, were not detected in the immediate vicinity of the discharge tube.

One materials-feed unit that was found to offer a practical solution for dropwise addition of liquids was a pressure-equalizing dropping funnel of approximately 100-cm^3 capacity installed at the input to the plasma reaction tube, see Figure 4.

The manipulative procedure involved, first, filling the dropping funnel with the liquid to be tested. The lowest Teflon needle-valve stopcock is in the closed position. The two remaining stopcocks are open. The entire system is evacuated to its minimum pressure, about 0.1 torr (mm Hg). For pure or solvent-free liquids, such as pure Malathion or polychlorinated biphenyls (PCB's), an ice water sample receiving trap is located directly below the plasma exhaust outlet, and liquid nitrogen-cooled traps are located downstream from the gas-sampling tube to collect condensable products and to minimize contamination of vacuum pump oil. Next, pressure is adjusted to the desired level by regulation of the main vacuum valve. A Tesla coil is generally used to ignite the discharge. When the Teflon needle valve is

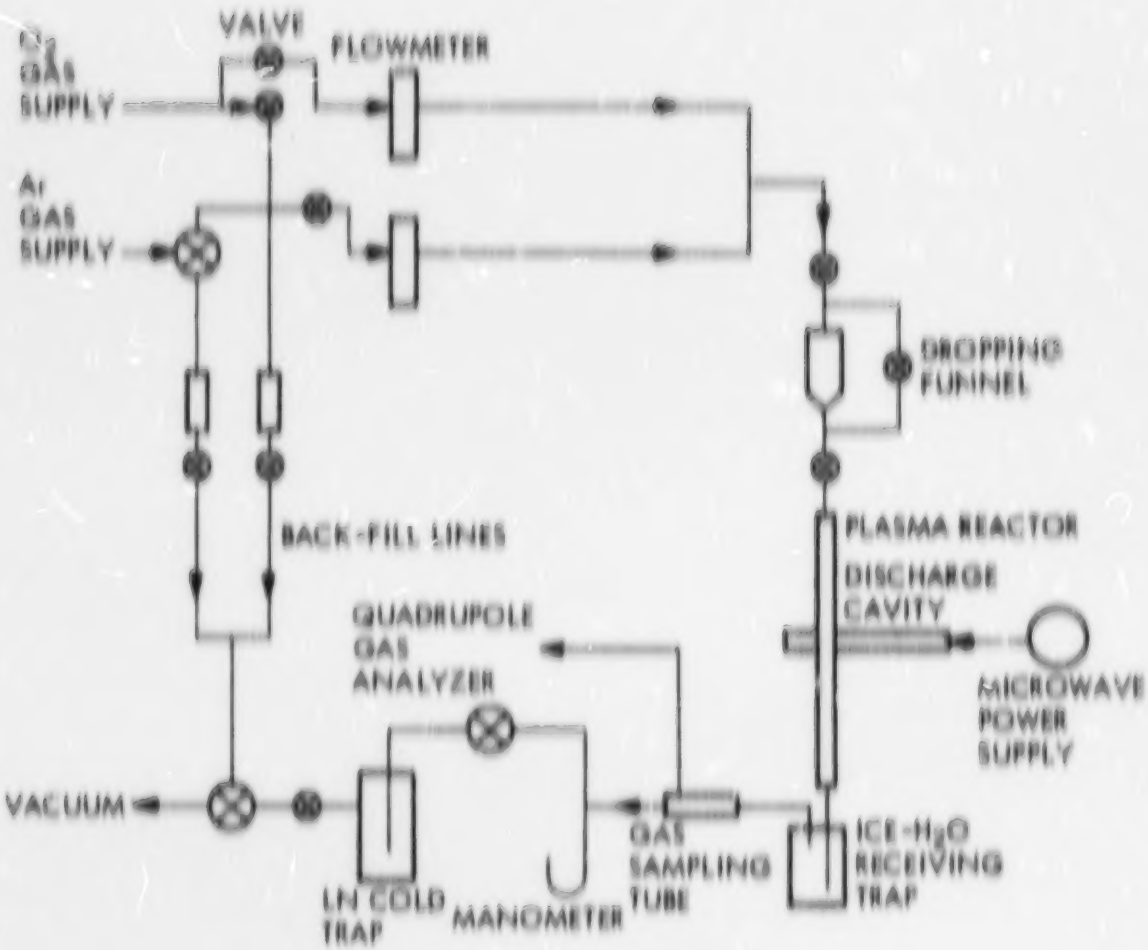


Figure 1. Schematic diagram of laboratory microwave plasma system

Figure 1. Laboratory Reverse Osmosis Pilot Unit

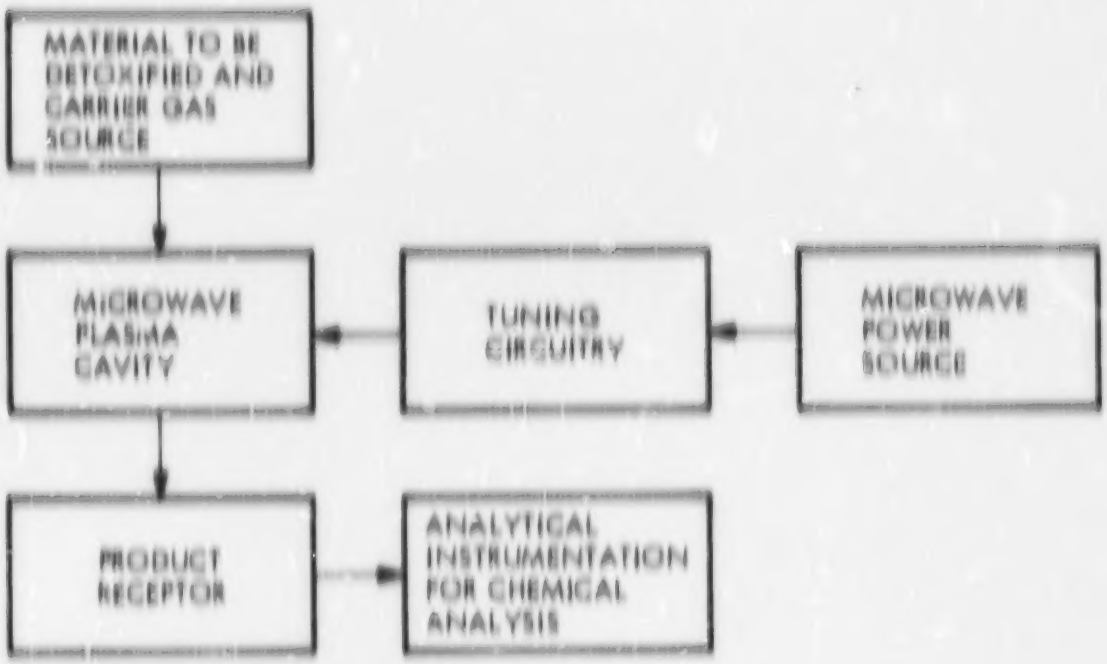


Figure 5. Block diagram of microwave plasma system and related components

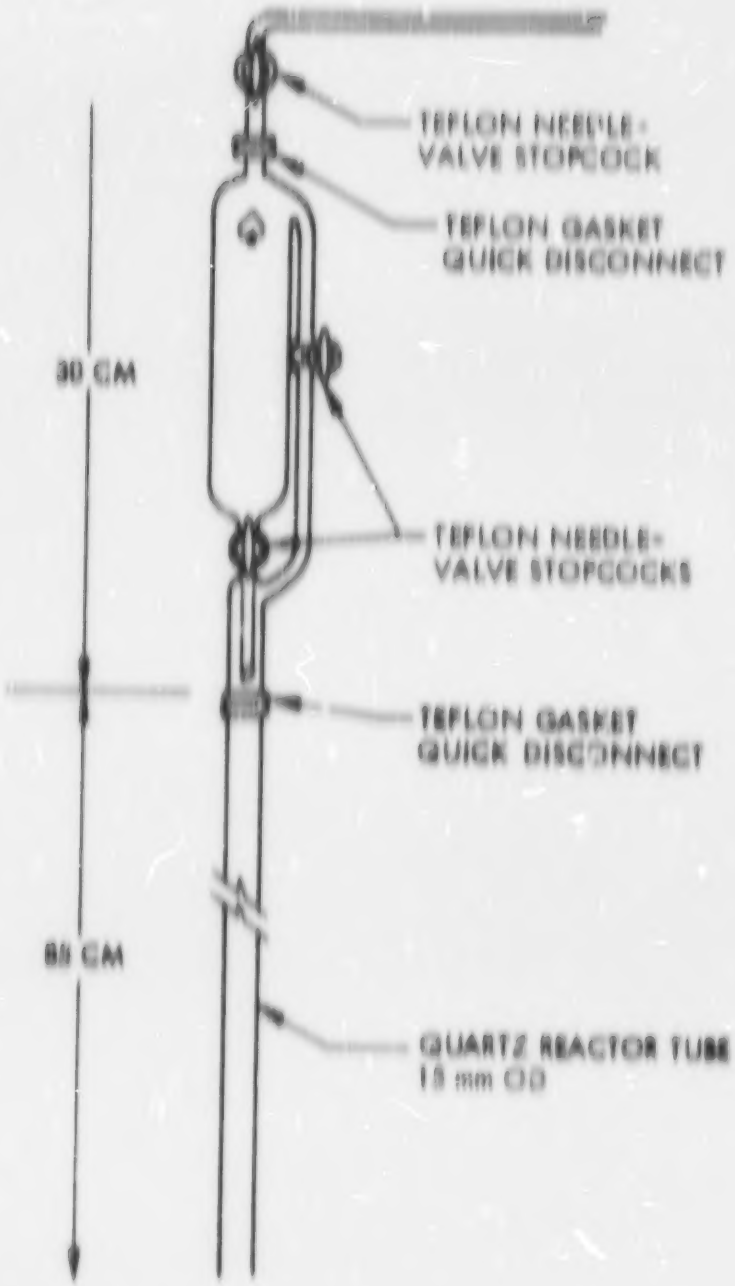


Figure 4. Reduced pressure liquid feed system – laboratory-scale

opened, small drops fall under gravity through the quartz reaction tube. Reaction product sampling is performed at the gas sampling tube, and the ice water and liquid nitrogen traps.

Calculations indicated that the rate of fall of a drop of pesticide at zero pressure through an average-size, 5-cm length plasma was 0.1 sec, using for the approximation $S = 1/2\ g\ \sigma^2$, where S is the distance traveled, g is the gravitation constant (980 cm/sec^2), and σ is time in seconds. The actual residence time σ will be shorter, since the liquid drops fall in the same direction as that of the carrier gas. However, since working pressures on the order of 10 to 100 torr are more the rule, the drag components associated with these pressures will lengthen the time over the estimated free-fall time. Therefore, the extent of change in σ is related, in addition to the size of the liquid drop, its density, and the operating characteristics of the carrier gas. Nevertheless, it was apparent that a method would be needed to increase the time for passage of the drop through the discharge.

The technique by which this was accomplished utilized a quartz mesh "basket" positioned at the center of the plasma zone. Quartz mesh fibers were loaded into the basket, and served as a contact area for the drops. The basket contained a sufficient number of holes to allow passage of the effluent reaction products, as shown in Figure 5. The process is continuous. The residence time has been estimated at 1/2 to 1 sec, the time for on-off occurrences of reaction flashes inside the plasma zone.

For gas feeds, such as methyl bromide, the dropping funnel was bypassed, and the pesticide was fed directly into the plasma.

With respect to additions of solids, this was deferred until the larger plasma system could be utilized. It was considered that development of a uniform method for feeding these materials into the narrow 15-mm o. d. reaction tubes would not be productive relative to the tasks prescribed for evaluation in the expanded-scale system.

3.2 EXPANDED-SCALE PLASMA SYSTEM

A primary objective of the program was the evaluation of the effectiveness of an expanded-scale microwave plasma system in processing hazardous organic compounds, wastes, and pesticides of current interest. In this regard, the reaction products were identified to determine whether the products were innocuous or toxic, and whether there was the possibility for recovery of useful materials as by-products.

The new microwave plasma applicator hardware and power supply equipment were supplied by Gerling Moore, Inc., Palo Alto, California, according to LPARL specifications. Figure 6 shows a schematic diagram of the microwave electronics and the associated process equipment. The principal difference between this system and the laboratory model is the method of application of power. In the laboratory unit, the applicator utilized a resonant cavity, Varian Model EC2-1083, which was fed by a single 2.5-kW power supply. In the expanded-scale unit, rectangular trough wave-

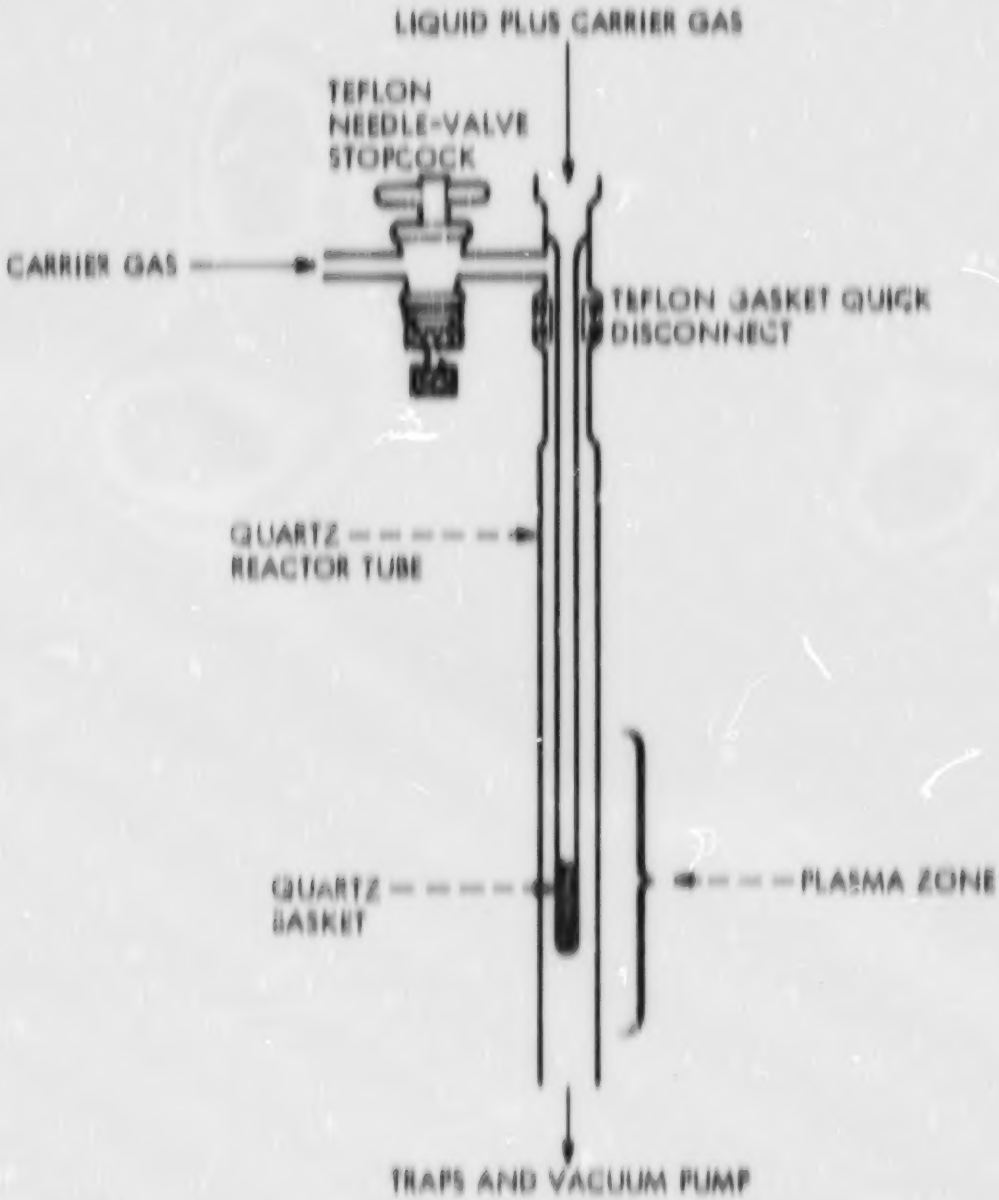


Figure 5. Quartz mesh basket within plasma reactor

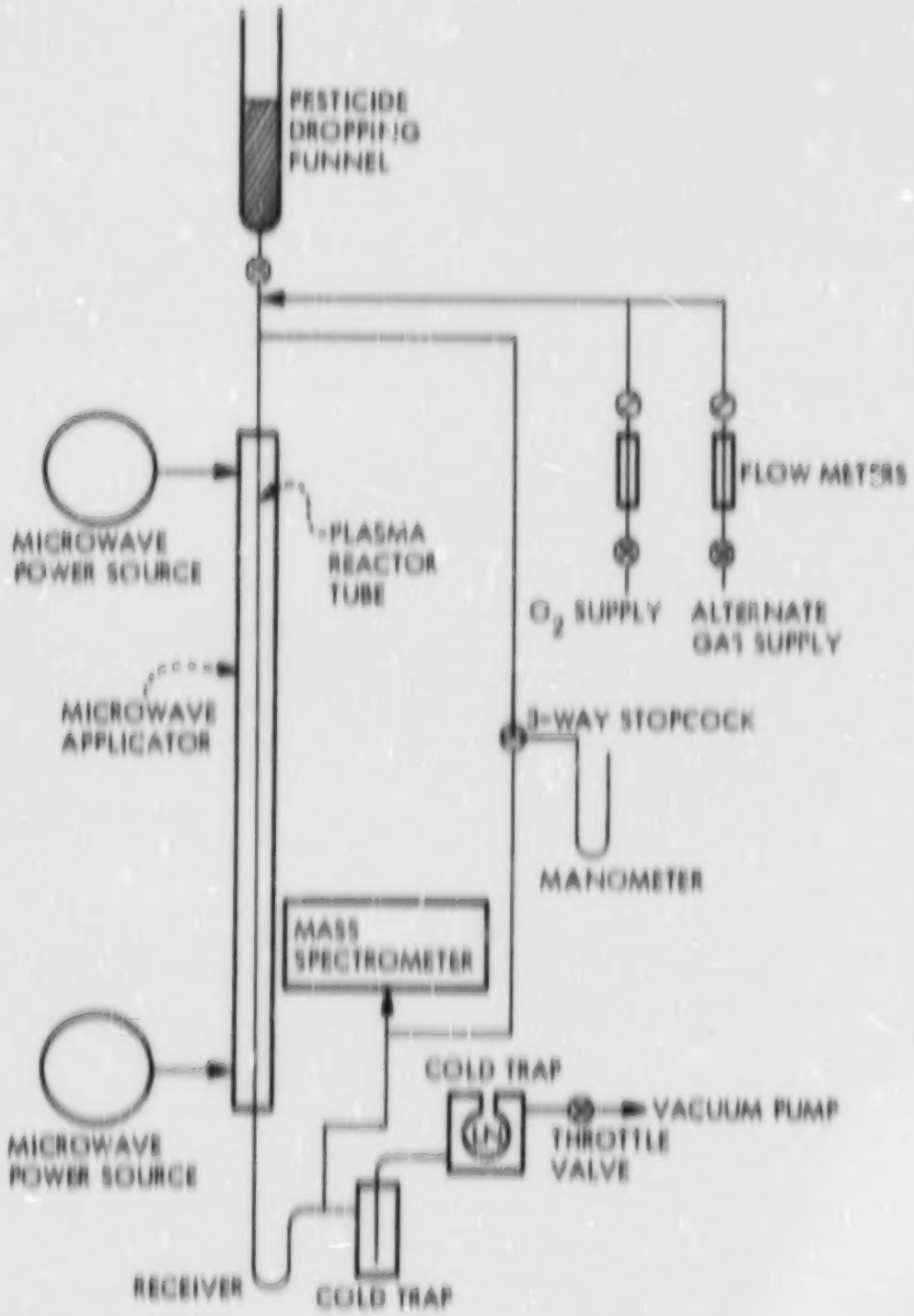


Figure 6. Expanded-scale microwave plasma system - schematic

guides were used. Two 2.5-kW power supplies fed the applicator, one supply for each ridge. A diagram of the microwave hardware and the associated electronics is shown in Figure 7.

In the design of the applicator, three lengths were chosen for the evaluations. These dimensions, exclusive of the two 21.6 cm (8.5 in.) end-mounted radiation cutoff sections, are listed as follows:

- Series A — 172 cm (68 in.)
- Series B — 92 cm (36 in.)
- Series C — 41 cm (16 in.)

The interior dimensions (i.d.) were the same for the three units: 21.6 cm (8.5 in.) x 5.7 cm (2.24 in.). The i.d. of the cutoff guides was 5.7 cm (2.24 in.) x 5.7 cm (2.24 in.). The ridges were 2.5 cm (1 in.) x 1.25 cm (0.5 in.) attached at the narrower dimension axially to the 5.7-cm section of the waveguide.

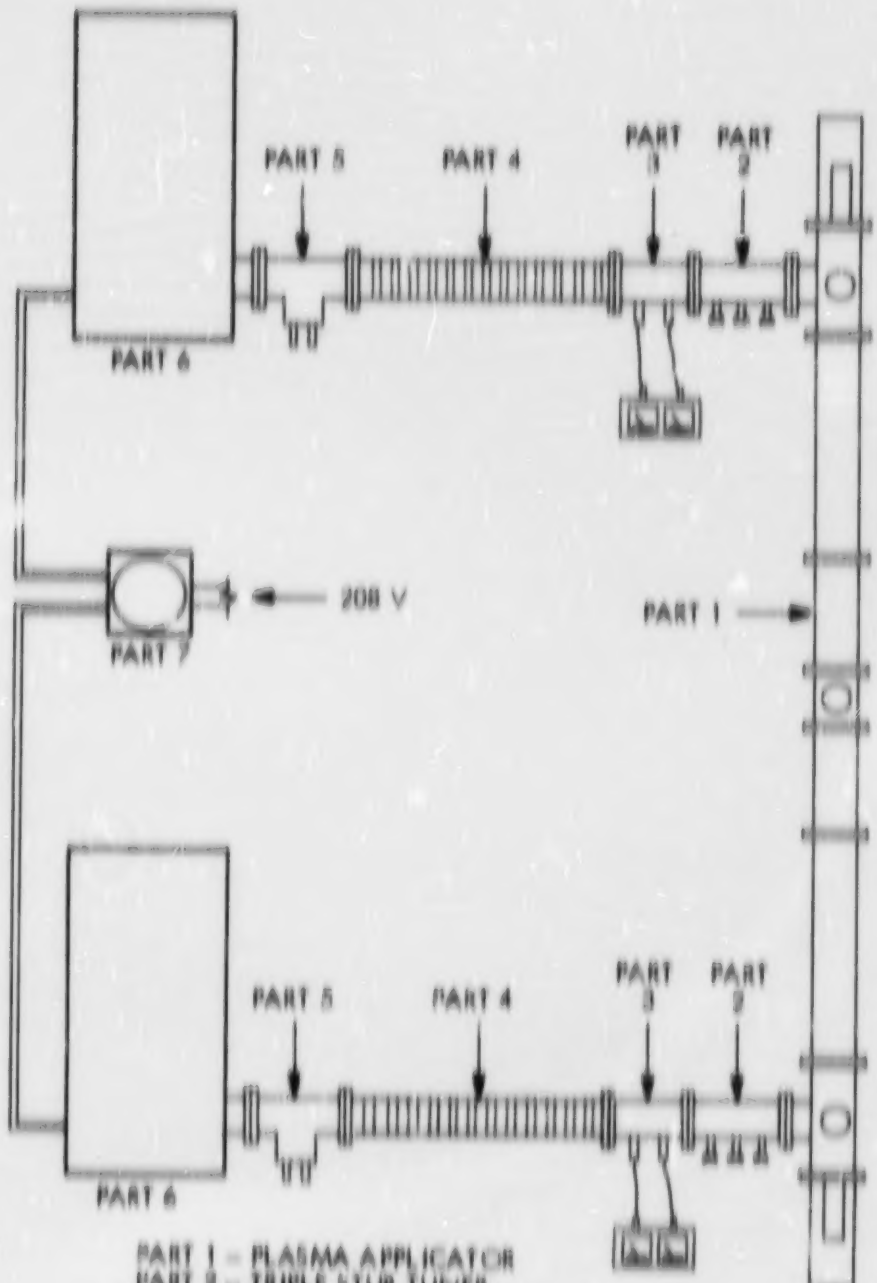
In Figures 8 through 10, the three systems are shown in assembly. Figure 8 shows the applicator slanted approximately 30 degrees. The variable positioning was feasible through use of the flexible waveguides from the power supplies. The master control unit, power supplies, etc., were installed in a single movable rack (Figure 11).

The reactor tubes were fabricated from transparent quartz with a 1.5 mm wall thickness, and an o.d. of 40 to 50 mm. Raschig rings, fabricated from quartz were used to fill the reactor in order to increase the residence time of the toxic materials in the plasma zone. The ring dimensions ranged from 8 mm o.d. x 4 mm length to 10 mm o.d. x 10 mm length. See Subsection 7.5.2 for development of optimum size of the rings.

The pesticide dropping funnel was a 2-liter version of the unit used for the laboratory-scale plasma tests (Figure 12). For relatively volatile solutions, a standard 250-cm^3 volumetric dropping funnel was used for feeding directly into the reactor, using atmospheric pressure above the solution (Figure 10).

The vacuum pump was a Welch DuoSeal Model 1397 oil-sealed two-stage mechanical pump with a free-air displacement of 425 liter/min. Various traps were installed between the reactor output and the pump for product collection and to maintain cleanliness of the pump oil. The output from the pump was passed through a stack exhaust to the exit port on the roof of the building.

The following procedure for operating the larger plasma systems was only slightly different from that of the laboratory unit. The system was evacuated initially to its minimum pressure, about 1 torr. With liquid-nitrogen or other low-temperature coolants in the trap condensers, the flow of oxygen was adjusted to maintain a pressure of about 10 torr. With all water and



PART 1 – PLASMA APPLICATOR
PART 2 – TRIPLE STUB TUNER
PART 3 – DUAL POWER MONITOR
PART 4 – FLEXIBLE WAVEGUIDE
PART 5 – 3-PORT CIRCULATOR AND WATER LOAD
PART 6 – VARIABLE POWER SOURCE AND CONTROL
PART 7 – 208 VOLT WATT-METER

Figure 7. Expanded-scale microwave reactor—hardware & associated electronics

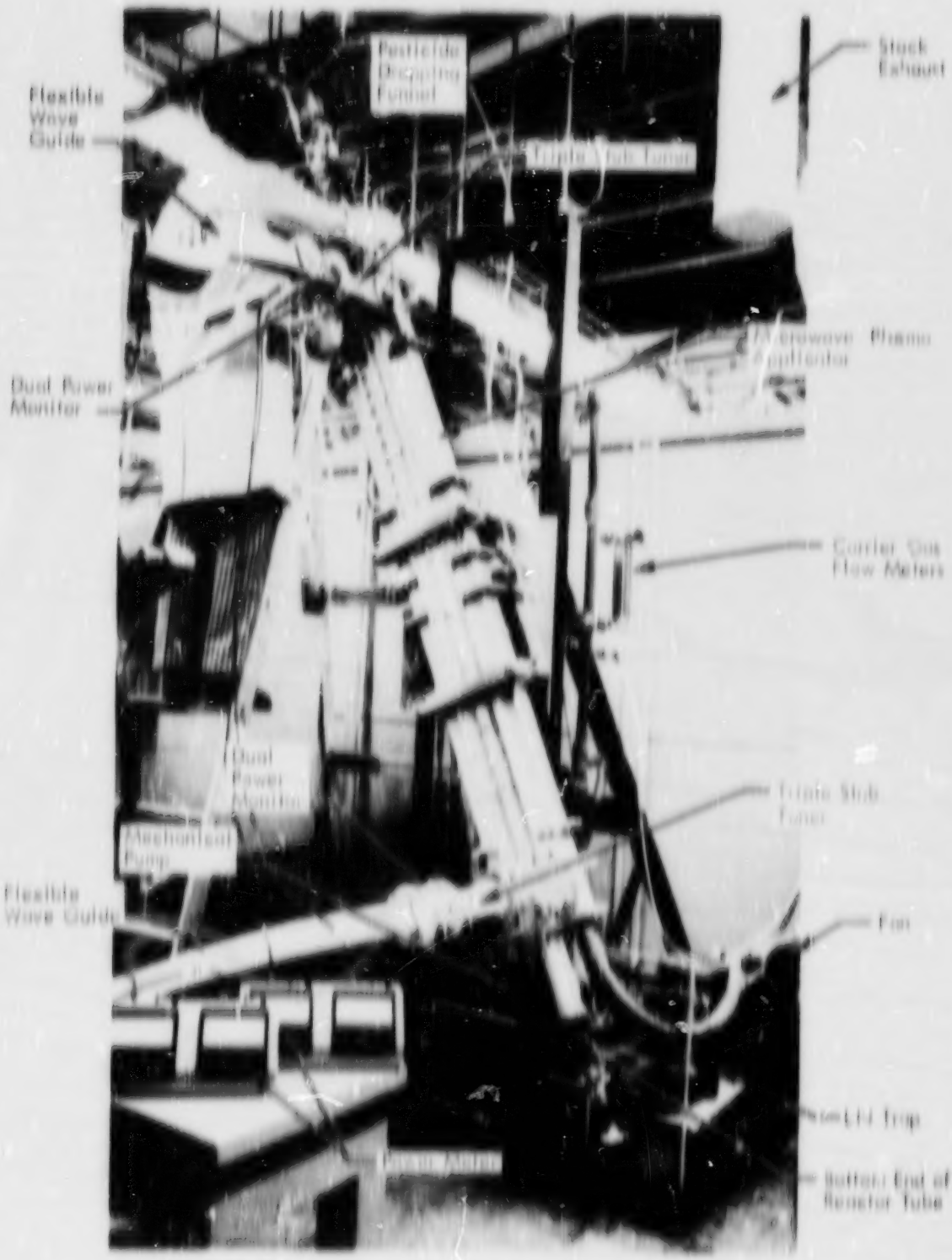


Figure 8. Series A microwave reactor system

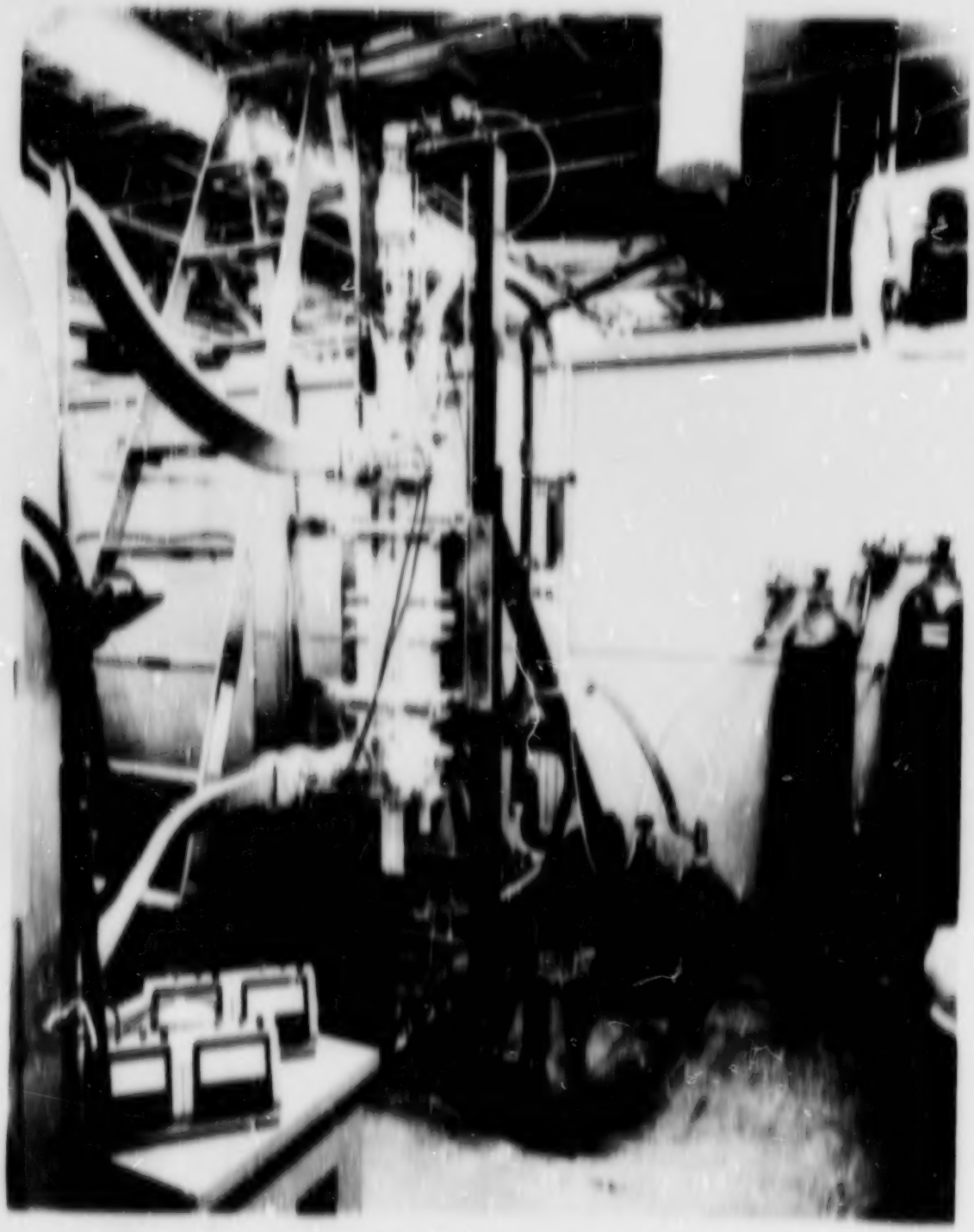


Figure 8. Series II microwave reactor system

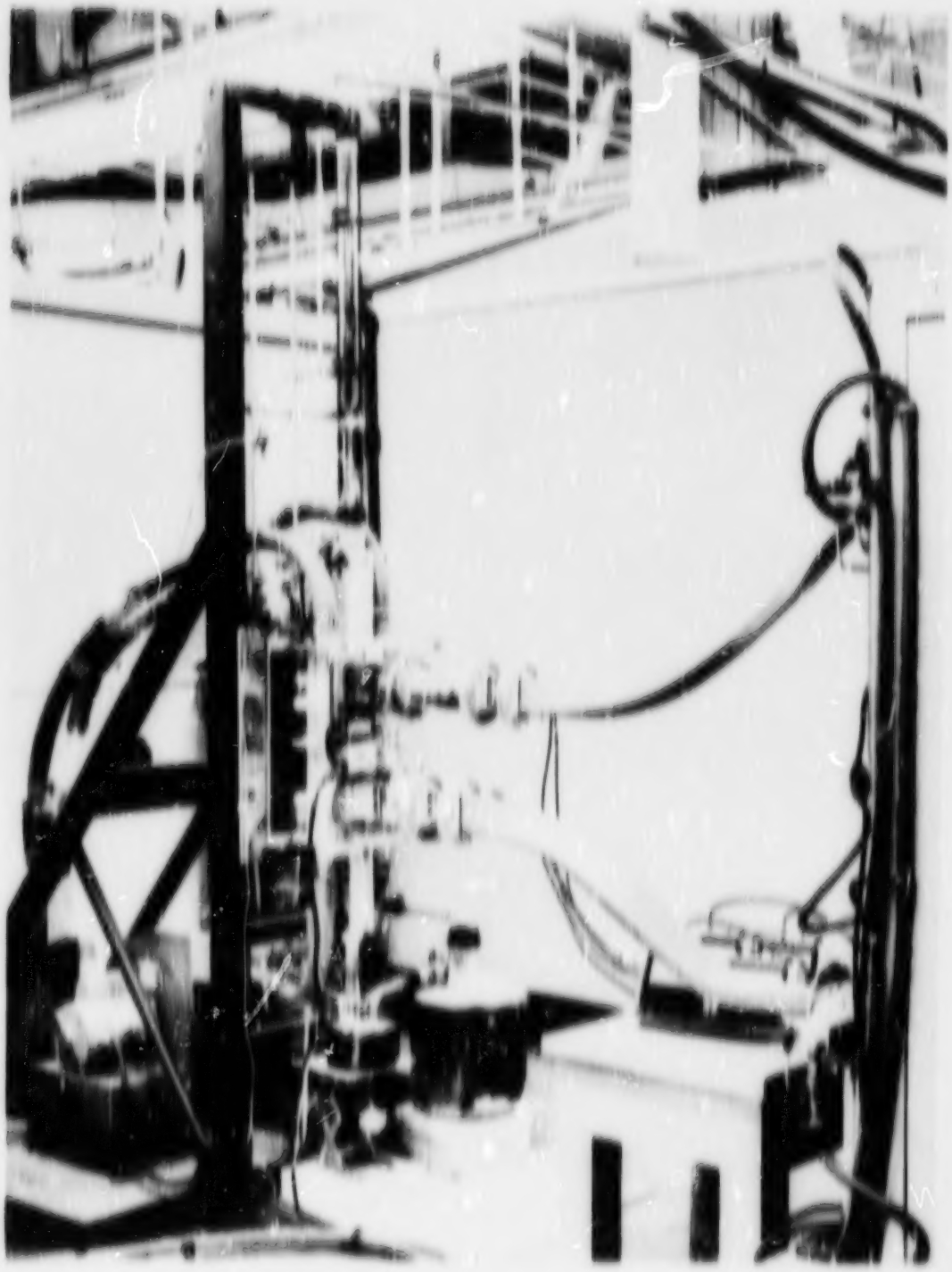


Figure 10. Series C microwave reactor system

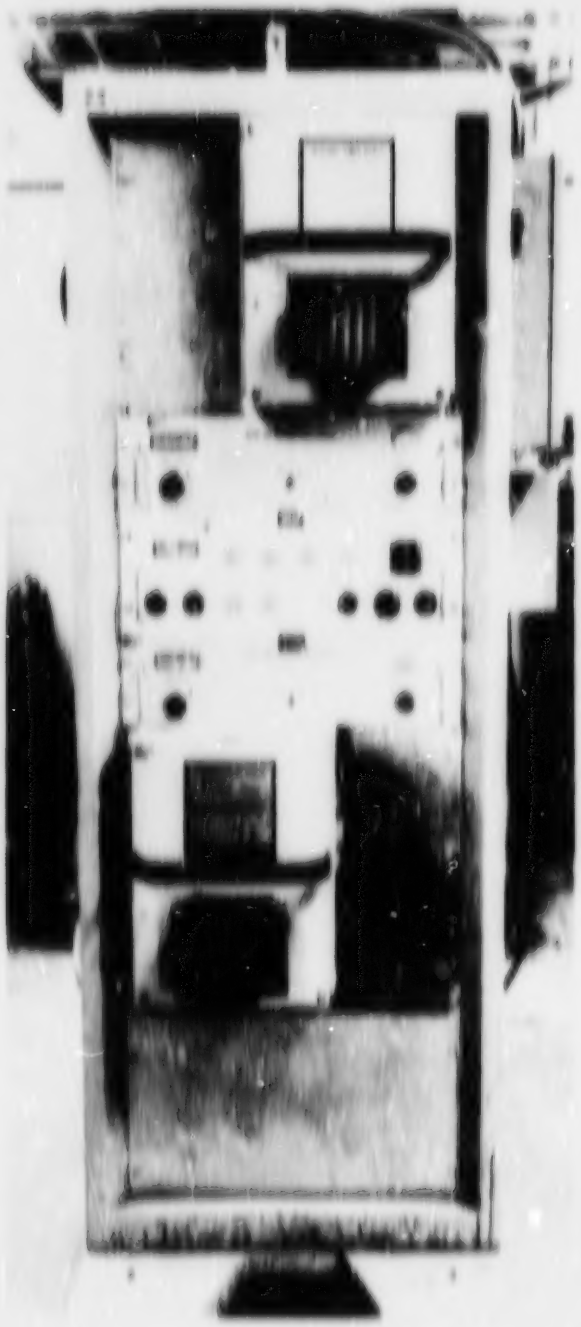


Figure 11. Microwave power sources and control console

Figure 18. Hazardous liquid injector system, 1 liter

air cooling on, the microwave power sources were activated. As soon as the plasma ignited, about 1 sec, the flow of oxygen was increased, and the pump throttle valve adjusted to achieve the desired combination of oxygen flow and pressure. The microwave power was set to the desired level, and the tuning controls adjusted to give minimum reflected power. During the procedure, a Holaday Model HI-1500-3 microwave radiation monitor was used to meter leakages in radiation,if any. Levels greater than 1/2 mW/cm^2 were not detected in the immediate vicinity of the discharge tube.

3.3 ANALYTICAL METHODS

Two principal methods were applied for waste analysis. Of these, mass spectroscopy yielded the maximum information on the identification of the gaseous products produced in the plasma. Infrared analysis was used for determination of effluent materials, which included solids and liquids, deposited in the product receiver traps. Gas chromatography and standard quantitative techniques for mass balance and heavy metals were adopted as required; details of these analyses are given in the section pertaining to the individual pesticides.

Mass spectrometric determinations were performed on a Varian Model 974-0002 residual gas analyzer, which includes an in-line continuous gas sampling system. Two ranges of atomic mass units (amu) were used as applicable to the specific pesticide or waste: 1 to 50 amu (for gases such as N_2, O_2, CO_2, CO, H_2O, CH_4, C_6H_6, etc.) and 1 to 350 amu maximum (for the detection of heavier gas, chlorinated hydrocarbons, etc.). Appendix A contains details of the instrumentation and sampling procedures.

Infrared spectrograms were determined on a Perkin-Elmer 621 IR spectrophotometer with a range of 4000 to 400 cm^{-1} (2.5 to 25μ). Materials to be analyzed were ground with KBr and compressed to form KBr pellets which were scanned over the prescribed spectrum.

SECTION 4

SELECTION OF PESTICIDES AND HAZARDOUS WASTE MATERIALS

The pesticides and hazardous wastes which were detoxified or decomposed by microwave plasmas are listed in Table 1, and classified as follows:

- Organophosphorus compounds
- Halogenated hydrocarbons
- Heavy metal compounds

The materials were tested in the form of a gas, as pure liquids, solvent solutions, aqueous slurries, and solid powder press cakes. Selections were made by EPA and LPARL personnel by mutual agreement on the basis of diversity in form and chemical constitution, and on the extent of the environmental problems which were associated with the materials to be detoxified. The properties and specifications of these materials are detailed in Appendix B.

In the following sections, a summary is presented of the conversion/detoxification data obtained from the oxygen plasma reactions performed in the laboratory and expanded-scale systems.

TABLE 1. PESTICIDES AND HAZARDOUS WASTE MATERIALS FOR DETOXIFICATION TESTS

Classification	Material	Form Tested	Manufacturer	Grade or Type
Organophosphorus Pesticide	Malathion	Pure Liquid	American Cyanamid	ULV
Chlorinated Hydrocarbon Waste	PCB's (Polychlorinated Biphenyls)	Liquid Mixture	Monsanto	Aroclor 1262 Aroclor 1254
Brominated Hydrocarbon Pesticide	Methyl Bromide	Commercial Gas	Matheson Gas	
Heavy Metal Fungicide	Phenylmercuric Acetate	Commercial Methanol Solution	Troy Chemical	Troysan PMA-30
Chlorinated Hydrocarbon Pesticide	Kepone	1. Commercial Powder 2. Aqueous Dispersion 3. Methanol Solution	Allied Chemical	80% Powder Concentrate Technical Grade

SECTION 5

RESULTS OF LABORATORY-SCALE OXYGEN PLASMA REACTIONS

The reactions in the laboratory plasma system, i.e., the system of 1-5 g/hr throughput, have illustrated the efficacy of the microwave plasma process on pesticides and related materials, using oxygen as carrier gas. Also evaluated were argon and hydrogen plasmas to determine their interactions, if any, with the toxic test materials.

On the basis of the observed formation of extremely offensive mercaptans from Malathion-type compounds in argon plasmas, and the projected formation of dimethylmercury from phenylmercuric acetate or other mercurials in argon and hydrogen plasmas, major efforts were applied to the development of an oxygen carrier gas technology. The reactions associated with the argon and hydrogen plasmas are given in Appendix C.

A summary of typical results from the laboratory unit is listed in Table 2.

5.1 MALATHION

"Cythion" ULV Malathion, manufactured by the American Cyanamid Company, was passed through 200 to 250 Watt oxygen plasmas at 100 to 120 torr, using the quartz basket technique. (See subsection 3.2 for a description of the technique.) With the exception of a white etch zone and a high viscosity water-white liquid that formed below the plasma, all the products were gases. Mass spectroscopy and gas chromatography indicated CO_2, CO, SO_2, and water as effluent gases. Infrared spectroscopy showed the liquid product to be phosphoric acid. Materials balances indicated that metaphosphoric acid was the probable material from which conversion to orthophosphoric acid in moist air occurred in 1 to 2 days.

Analysis for Malathion in the liquid reaction product was carried out colorimetrically (10). Percent conversion was 99.98 + percent based on 0.018 percent Malathion determined.

5.2 POLYCHLORINATED BIPHENYLS (PCB'S)

Monsanto Aroclor 1242 liquid was passed through a 250 Watt oxygen plasma at 100 torr pressure. Mass balance weighings showed no liquids attributable to the starting material. All the products of decomposition were gases. On the basis of control runs in the absence of the plasma

TABLE 2. REPRESENTATIVE LABORATORY-SCALE OXYGEN PLASMA REACTIONS

Pesticide/ Waste	Run No.	Microwave Plasma Power (W)	Pressure (torr)	Conversion (%)	Reaction Products
Malathion "Cythion" ULV	28-40	200-250	100-120	98.98+	SO_2, CO_2, CO, H_2O, HPO_3 or H_3PO_4 *
PCB, Aroclor 1242	28-58	250	100	99.9+	CO_2, CO, H_2O (Cl_2), $COCl_2$*
Methyl Bromide	28-94	300-400	50	99*	CO_2, CO, H_2O, Br_2, BrO_2*
Phenylmercuric Acetate, "Troysan" PMA-30	28-142	225-280	120	99.9	Hg, CO_2, CO, H_2O

*See text.

reaction, percent conversion was calculated at greater than 99.9 percent. Gas products were identified as CO_2, CO, H_2O, Cl_2O, and $COCl_2$. It will be of interest to note that the latter gases, chlorine oxide and phosgene, were not observed in the expanded-scale plasma reactions; rather, hydrogen chloride was the principal Cl-containing product (see section 6.2).

5.3 METHYL BROMIDE

Gaseous methyl bromide was passed through 300 to 400 Watt oxygen plasmas at 50 torr pressure at 2 to 3 g/hr. The products of reaction were CO_2, CO, H_2O, and Br_2. Oxides of bromine were found in the liquid nitrogen traps, but were not otherwise produced at ambient temperatures. Quantitative analysis of the plasma reactions was performed by mass spectrometer, in which the ratios of CH_3Br response heights before and during the plasma reactions were compared. (See Appendix A, Mass Spectra). Conventional analytical methods were precluded because of the toxicity of the methyl bromide gas. Decomposition was greater than 99 percent, which is the limit of precision for the method.

5.4 PHENYLMERCURIC ACETATE

Commercial Troysan PMA-30 solution (30 percent phenylmercuric acetate, approximately 70 percent methyl alcohol, plus ammonium acetate) was passed through a 225 to 280 Watt plasma at 120 torr pressure. Metallic mercury was observed as a metallic mirror on the glass tubing downstream from the plasma zone. Material balance indicated 99.9 percent decomposition to mercury metal. Mass spectroscopy showed the products formed in addition to Hg were H_2O, CO_2, and CO. There was no evidence of dimethyl mercury or other organomercurials.

SECTION 6

RESULTS OF EXPANDED-SCALE OXYGEN PLASMA REACTIONS

The expanded-scale plasma system is defined as the equipment shown in Figures 8 through 11 which resulted in detoxification yields of 410 to 4200 g (1 to 7 lb) per hr.

Three microwave power applicators and three equivalent-size quartz reactor tubes were used in the evaluations. During the initial runs, the Series A 2.7-liter applicator was used for oxygen plasma decomposition of PCB, Aroclor No. 1248. It was determined that the liquid had been decomposed and that one of the reaction products -- a black, soot-like deposit which coated the product receiver -- contained no PCB, as determined by infrared spectroscopy. Several additional runs, in which feed, pressure, and absorbed power were varied, indicated, however, that the Series A system was too large in volume for the power available. As a result, the Series B and C applicators, 1.48 and 0.85 liters, respectively, were used for all detoxification reactions which are described in the following subsections, and detailed in Table 3. It may be readily concluded, from the results of those evaluations, that the Series C reactor yielded the highest throughput, the highest percentage of conversions, and the lowest costs, as calculated in Section 6.6.

6.1 MALATHION

"Cythion" Malathion ULV liquid was drop-fed onto a porous, dielectrically heated quartz wool bundle positioned at the top applicator input to the plasma zone. By this means, in a similar mechanism to that which was used in the laboratory-scale system, large numbers of smaller droplets or vaporized particles were produced within the matrix of the heated wool, and propelled by the carrier gas through the plasma. Reaction products were gaseous sulfur, SO_2, H_2O, CO, CO_2, and acetylene, plus a liquid phosphoric acid. Deposits of a dark yellow-brown sulfur product mixed with a clear, water-white high-viscosity liquid dropped gradually down the sides of the reactor into the receiver. No carbon or any products resembling the starting material were observed. Analysis of the liquids from two reactions gave results of 12 ppm and < 1 ppm Malathion, respectively, or conversions of 99.9988 and 99.9999 + percent.

6.2 POLYCHLORINATED BIPHENYLS (PCB'S)

Runs 31-8, 31-10, and 31-62 yielded HCl, CO, CO_2, and H_2O as determined by mass spectrometer. No Cl_2O or $COCl_2$ was observed. There

TABLE 1. SUMMARY OF EXPANDED-SCALE OXYGEN PLASMA REACTIONS

Pesticide/Waste	Run No.	Reactor Series	Microwave Power (kW)	Feed Rate g/hr (lb/hr)	Pressure (torr)	Oxygen Gas Flow (liters/hr)	Reactor Packing	Conversion (%)
Malathion "Cythion" ULV	32-16	B	3.7	504(1.1)	28-46	361	Wool Plug[a]	99.9988
Malathion "Cythion" ULV	31-46	B	4.7	480(1.1)	26-38	480	Wool Plug	99.9364
PCB Aroclor 1242	31-8	B	4.6	2704(6.0)	17-35	323	Wool Plug	99
PCB Aroclor 1242	31-10	B	4.2	492(1.1)	19-36	395	Wool Plug	98
PCB Aroclor 1254	31-42	B	4.5	2068.4)	13-25	380	Solid Rings[a]	99
PMA Troysan PMA-30	31-88	C	4.6	1020(2.25)	120-140	960	Raschig Rings[a]	Complete ation, 99.99[b]
PMA Troysan PMA-30	31-108	C	4.0	2380(5.25)	100-120	792	Raschig Rings	Complete ation, 99.99
PMA Troysan PMA-30	31-110	C	4.3	2950(6.5)	100-120	792	Raschig Rings	Complete ation, 99.99
Kepone 80/20 20% Methanol Solution	38-30	C	4.6	(a)	54	720	Raschig Rings	99
Kepone 80/20 10% Solids Aqueous Slurry	38-36	C	4.2	-	40	None	Raschig Rings	99
Kepone 1- to 3-g Solid Discs	38-38	C	4.6	-	7	0C	Raschig Rings	99

(a) Quartz (b) see text

was formation of soot in the product receiver; infrared analysis gave no indication of PCB residues. It was determined, however, that at throughput levels of about 1 kg/hr in the B reactor, complete reactions had not occurred. This was determined by infrared analysis of the black tar-like liquid products in the receiver trap which indicated the presence of PCB starting material.

6.3 PHENYLMERCURIC ACETATE

Troysan PMA-30 was passed through the Series C reactor in several runs to determine the effect of the shortened length of the reactor, and the presence of quartz Raschig rings in the reactor tube. The reaction was considered complete; i.e., no starting material passed through the plasma zone, if methanol peaks were not found by mass spectroscopy in the effluent gas.

A series of reactions showed that at a throughput of 3600 g/hr (8 lb/hr), small amounts of methanol solvent were detected in the gaseous effluent. This indicated that under the conditions of this series, between 7 and 8 lb/hr can be considered for effectively complete detoxification/destruction of PMA-30. The principal gases of the reaction were CO_2, CO, and HgO. Metallic mercury was deposited in the traps downstream from the plasma. Additional information is given in subsection 7.3.4. It is also of importance to note that no organomercurials were detected by the mass spectrometer.

6.4 KEPONE - A "REAL WORLD" MIXTURE

A commercial, clay-supported mixture, Allied Chemical 80-percent Kepone concentrate, Code 8406, was used for all tests. Approximately 250 g was available, which was converted as needed into water slurries, methanol, and methanol/acetone solutions, and solid press cakes. The solid press cakes were prepared by compressing 2-3 g batches of Kepone 80/20 in a die under 1000 psi pressure. The discs, which required strong finger pressure to fracture, were placed at the top of the Raschig ring area in the plasma reactor tube before the plasma was ignited. It was observed visually that breakdown of the solids occurred in 10 to 30 seconds, depending on the flow of oxygen and the pressure within the reactor. An extrapolation of a 3-gram batch decomposition in 15 seconds yields 720 g/hr or 1.6 lb/hr detoxified. The gaseous reaction products were CO_2, CO, HCl, and HgO. Hexachlorobenzene, phosgene, or chlorinated hydrocarbons were not detected using a combination of techniques involving infrared and mass spectroscopy. Because of the limited quantity of the starting material, the reactions were not optimized with respect to throughput. Nevertheless, 3 kg/hr (7 lb/hr) are considered to be well within the capabilities of the system. Safety and handling precautions were observed meticulously for the Kepone experiments. All solution and dispersion operations were carried out in a chemical hood which had a linear velocity of 100 feet per minute at the air inlet. Press cake operations performed in the open laboratory utilized a 4-in.-diameter suction tube which was connected to the chemical hood. The tube acted as a vacuum cleaner-type device to prevent dust from contaminating the laboratory area; and decontamination of residual solids were carried out by dissolving in acetone which was subsequently stored in separate waste bottles. Paper wipes were also stored separately.

6.5 STEAM PLASMA DETOXIFICATION OF PMA-30

Toward completion of the program, several successful exploratory experiments using steam instead of oxygen were performed in the expanded-scale Series C plasma unit. PMA-30 was evaluated in this reactor.

The major products of the discharge were CO_2, CO, H_2O and mercury metal. Very few, if any, signs of lower C_1 to C_3 hydrocarbons were observed. There was also no sign of the PMA methanol solvent. Thus, the water plasma decomposition of PMA appeared the same as that which occurred in the oxygen plasma.

Because of the potential for significant cost savings and the fact that steam, when condensed, will develop its own vacuum, this additional technology is considered to be of significant promise. In addition, when the water vapors condense below the plasma zone, dissolution or entrapment of acid gases can occur. The dissolved materials may then be treated with caustic by standard methods. It is therefore planned to include steam as carrier gas in future microwave plasma investigations at the pilot- and demonstration-levels.

6.6 PROCESS COSTS CALCULATED FOR PMA-30

For the initial detoxifications in the expanded-scale plasma system, a cents-per-pound figure for electrical power and carrier gas costs was calculated. It was considered appropriate that the calculation be made exclusive of capital investment for later comparison with pyrolysis, high temperature, and other forms of specialty incineration as data on those processes became available. This type of information was derived for the conversion of phenylmercuric acetate pesticide. It is presented in Table 4.

For the determination of process costs for future 50 to 100 lb/hr demonstration-scale plasma systems, an accurate assessment is at this time replete with difficulties. Nevertheless, where the object is to show, in principle, the economic viability of the approach, it is possible to calculate values which can be derived from known process variables and estimated carrier gas, electrical, and related costs.

The material chosen for the calculation was phenylmercuric acetate (PMA), first, because it was considered refractory or difficult to decompose completely and, second, because it has the significant advantage of recoverability of its metallic mercury values.

The following assumptions are listed below as part of the estimated costs:

(1) Electrical costs are $0.012/kWh, industrial usage.

(2) Liquid oxygen costs are $0.005/SCF, large volume usage. Add $3000/yr storage fee.

TABLE 4. ELECTRICAL AND CARRIER GAS COSTS FOR PLASMA REACTIONS IN SERIES C REACTOR EXPANDED-SCALE SYSTEM

Run No.	Material	Carrier Gas[a]	Effective (Absorbed) Microwave Power (kW)	Feed Rate [g/hr (lb/hr)]	Carrier Gas Flow [std liter/hr (SCFH)]	Gas Cost ($/lb)	Total Power Consumed (kWh/lb)	Power Cost ($/lb)[b]	Total Cost ($/lb)
31-88	PMA-30	O_2	4.6	1020(2.25)	340(340)	0.18	4.7	0.06	0.24
31-108	PMA-30	O_2	4.0	2380(5.25)	793(793)	0.064	1.9	0.023	0.087
31-110	PMA-30	O_2	4.3	2950(6.5)	793(265)	0.054	1.6	0.019	0.07

[a] O_2, $0.012/ft^3$

[b] kWh, $0.012, Industrial Usage.

(3) Steam costs are $5.00/1000 lb.

(4) Labor costs are one-half man per automated unit, i.e., one man operates two units, $12/hr.

(5) In the case of PMA, the credit for metallic mercury is $1.50/lb. This is based on a requirement for future purification. At present, the purity of the recovered metal has not been determined. A more pure product obviously has greater value, up to $4/lb.

(6) The estimate for capital costs is $100,000.

It may appear at this time that 50 to 100 lb/hr are low values when compared with municipal waste processes. However, the detoxification of even a small, 10-pound batch of a highly toxic or dangerous substance can give great concern to those who are responsible for its safe disposal.

In the following calculation, a standard 330-day/year, three-shift operation is assumed. PMA-30 throughput is 50 lb/hr, or 400,000 lb/yr. The process costs related to PMA-30 on a per-pound basis are as follows:

- Oxygen 4.3 SCF
- Steam 1.5 lb
- Electrical 1.8 kWh

Calculated total process costs are listed below:

	Oxygen	Steam
Variable Costs		
Operating Labor	$ 47,520	$ 47,520
Maintenance (4% of investment)	4,000	4,000
Oxygen or Steam	11,000	1,200
Electricity	7,680	7,680
Total Variable Costs	$ 70,800	$ 60,400
Fixed Costs		
Taxes and Insurance (2%/yr)	$ 2,000	$ 2,000
Capital Recovery (10 yr - 10%)	16,250	16,250
Total Fixed Costs	$ 18,250	$ 18,250

	Oxygen	Steam
Total Annual Costs	$ 89,050	$ 78,650
Total Income From Recovered Mercury	$108,000	$108,000
Total Net Profit	$ 18,950	$ 29,350
Net Profit Per Pound Treated	$ 0.047	$ 0.073

For detoxification of materials, such as Malathion or polychlorinated biphenyl wastes, where little or no useful by-products are recoverable, the costs may be higher. In oxygen and steam plasmas, for example, the costs per pound are calculated as $0.22 and $0.30, respectively.

It should be noted that as microwave power technology advances, the electrical costs should decrease as the result of improvements in the coupling of microwave power to the plasma reactors. The potential for steam plasmas with their low cost, plus their capability to form their own vacuum, is readily apparent, and can therefore be considered for further reductions in electrical power requirements.

The above data have been derived for a permanent-type disposal center, which may then be compared with other methods operating at similar levels of throughput. The costs associated with projected mobile, or back-of-truck type, detoxification units will vary, depending on the initial capital costs, which should be lower, and labor costs, which may be higher per unit. The latter will be dependent in part on the distance to the user's site as well as the toxicity of the materials to be treated.

SECTION 7

DISCUSSION OF RESULTS

An overview of the chemistry of microwave plasma detoxification and process variables as determined during the first year of the program is presented in the following subsections.

7.1 INTERPRETATION

- Microwave detoxification, using oxygen plasmas, has been successful and practical for all pesticides and hazardous wastes tested to date. These include Malathion, polychlorinated biphenyls, methyl-bromide gas, phenylmercuric acetate, and Kepone.

- Optimization of plasma conditions was performed for the refractory organomercurial, phenylmercuric acetate. As a result of varying the several parameters affecting the detoxification efficiency, decomposition was 3.2 kg/hr (7 lb/hr), yielding principally gaseous CO_2, CO, H_2O, and metallic mercury. The mercury has a known cost recovery value, thereby resulting in low or nonexistent operating costs for that particular material.

- Oxygen plasma reactions were uniform in their production of gaseous oxides of carbon, water, and acidic gases.

- Pure liquids, solutions, aqueous slurries, and powders as press cakes were decomposed by oxygen plasmas. The only differences in response were associated with the methods of addition used for the respective materials. The chemical reactions were effectively identical.

- Further process cost reductions are potentially feasible through the use of steam plasmas, which, in addition to low costs relative to oxygen, can also develop their own reduced pressures in the plasma reactor.

7.2 CHEMISTRY OF OXYGEN PLASMA REACTIONS

7.2.1 Malathion – Oxygen Plasma Reactions

Complete oxidation of Malathion in the laboratory-scale system yielded colorless gases and a water-white liquid: SO_2, CO_2, CO, H_2O, and phosphoric acid products. Several equations may be written for the reactions. For simplicity, only CO_2 is included.

$$C_{10}H_{19}O_6PS_2 + 15O_2 \rightarrow 2SO_2 + 10CO_2 + 8H_2O + H_3PO_4 \text{ (orthophosphoric acid)}$$

$$C_{10}H_{19}O_6PS_2 + 15O_2 \rightarrow 2SO_2 + 10CO_2 + 9H_2O + HPO_3 \text{ (metaphosphoric acid)}$$

$$2C_{10}H_{19}O_6PS_2 + 30O_2 \rightarrow 4SO_2 + 20CO_2 + 17H_2O + H_4P_2O_7 \text{ (pyrophosphoric acid)}$$

$$2C_{10}H_{19}O_6PS_2 + 30O_2 \rightarrow 4SO_2 + 20CO_2 + 19H_2O + P_2O_5 \text{ (phosphoric anhydride)}$$

Starting with 3.7 g Malathion added, the stoichiometry indicates the following:

H_3PO_4	0.80 g
$H_4P_2O_7$	0.73 g
HPO_3	0.65 g
P_2O_5	0.58 g

The experimentally determined value, twice run, was 0.66 g. Although pyrophosphoric acid has been detected in air-oxidation incineration reactions of phosphorus-containing materials, metaphosphoric acid appears to have been produced in this system. The difference in phosphoric acid identities may be related to the differences in the effective temperatures of the two reactions, and, consequently, their rates of formation in air (incineration) versus pure oxygen (plasma process). On further exposure of the phosphoric acid liquid to laboratory air for several days, orthophosphoric acid was determined by infrared spectroscopy to be the final product.

In the expanded-scale Series B system, some sulfur and small amounts of acetylene were observed in addition to CO_2, CO, H_2O, and SO_2. This is attributed to the incomplete oxidation of the starting material, since the system had not yet been optimized. It would not be considered difficult now to obviate acetylene or sulfur under currently optimized conditions in the Series C reactor.

7.2.2 PCB – Oxygen Plasma Reactions

Reactions in the laboratory-scale system yielded CO_2, CO, H_2O, Cl_2O, and $COCl_2$, whereas in the expanded-scale system, Series B, no Cl_2O or $COCl_2$ was observed. Instead, HCl was the Cl-bearing product detected, plus a soot-like deposit in the product receiver. It is probable that the

following type of reaction occurred in the reactor configuration used at the time:

$$C_{12}H_7Cl_5 + 11/2O_2 \rightarrow 2H_2O + 5CO_2 + 5CO + 6C(soot) + 3HCl$$

Optimization of the reaction in the Series C reactor should result in the disappearance of soot, and an additional formation of CO_2, etc.

7.2.3 Methyl Bromide - Oxygen Plasma Reaction

In the laboratory-scale system, oxidation yielded CO_2, CO, H_2O, and Br_2 as principal products, with some BrO_2 and/or Br_2O formed inside the liquid nitrogen traps. The principal reaction may be written as follows:

$$4CH_3Br + 7O_2 \rightarrow 2Br_2 + 4CO_2 + 6H_2O$$

Side reactions involving Br_2 and H_2O may have produced HBr and HOBr.

7.2.4 Phenylmercuric Acetate - Oxygen Plasma Reactions

In both the laboratory-scale and expanded-scale plasma systems, the major products were CO_2, CO, H_2O, and mercury metal. Minor amounts of lower molecular weight hydrocarbons were observed in the expanded-scale system. The formation of metallic mercury may be explained by postulating HgO as an intermediate in the plasma reaction, followed by its decomposition. The dissociation pressure of HgO to give Hg metal and O_2 is a few torr at 440°C (11). Thus, Hg metal can be produced as follows:

$$1)\ C_8H_8O_2Hg + 19/2O_2 \rightarrow HgO + 4H_2O + 8CO_2$$

$$2)\ HgO \xrightarrow{400\text{-}500°C} Hg + 1/2O_2$$

Addition of 1) and 2) yields:

$$C_8H_8O_2Hg + 9O_2 \rightarrow Hg + 8CO_2 + 4H_2O$$

Oxidation of methanol is considered to follow the usual mechanism to CO_2 and H_2O, depending on the quantity of oxygen available.

7.2.5 Kepone - Oxygen Plasma Reactions

The plasma reaction products of 30 percent Kepone-methanol and Kepone-methanol/acetone solutions in the expanded-scale system were CO_2, CO, H_2O, and HCl. Hexachlorobenzene, phosgene, or chlorinated hydrocarbons were not detected. Reactions in an oxygen plasma may therefore be written:

$$C_{10}Cl_{10}O + 7O_2 \rightarrow 5CO_2 + 5CO + 5Cl_2 \qquad (1)$$

$$2CH_3OH + O_2 \rightarrow CO + CO_2 + H_2O \qquad (8)$$

Reaction of Cl_2 with the H_2O from the methanol reaction produces HCl and HClO; since the latter is unstable, it decomposes to HCl and oxygen.

It is of interest to note that the time periods for decomposition of small 5 g, 80/20 Kepone press cakes within the plasma zone were 10 to 30 sec; the actual values depended on the surface area of the solids, the flow of oxygen, and the pressure within the reactor.

Percentage conversions are listed at >99 percent. The values are based on analysis of the effluent products. Absence of Kepone or hexachlorobenzene in the receiver, or any low molecular weight chlorinated hydrocarbons in the gas effluent denotes a greater than 99 percent conversion. Infrared spectrograms of Kepone extracted with acetone and its oxygen plasma reaction product are shown in Figure 13.

7.3 EVALUATION OF ANCILLARY EQUIPMENT

Four specific unit processes were developed and tested for use in the expanded-scale plasma detoxification system, as follows:

- Materials feed techniques
- Packed bed technology
- Reduced pressure systems
- Analytical processes

7.3.1 Materials Feed Techniques

Several techniques were evaluated to optimize as far as practicable the desired materials introduction processes. These included one- and two-fluid spray nozzles, in which the feed stock was introduced upwards from bottom to top in order to maximize residence time and to minimize gravity effects. No fine-spray system was found completely satisfactory, since little or no liquid spray flare-out can be tolerated below the plasma zone in the waveguide cutoff. If flare-out is permitted, thermal decomposition may occur in the cutoff, and the chemical identity of the products as well as the material balance becomes difficult or impossible to evaluate. Custom-fabricated two-fluid nozzles are now being designed to avoid these problems, which can become more significant when larger quantities of materials are detoxified.

The most successful technique was a vacuum-equalized liquid-feed system (Figure 14) into which several Teflon needle valves were constructed for improved drop-size control. This technique was used for gravity feeding PCBs and PMA-30 solutions. For feeding Kepone solutions and water slurries, the use of a volumetric buret was adequate; the feed was kept at

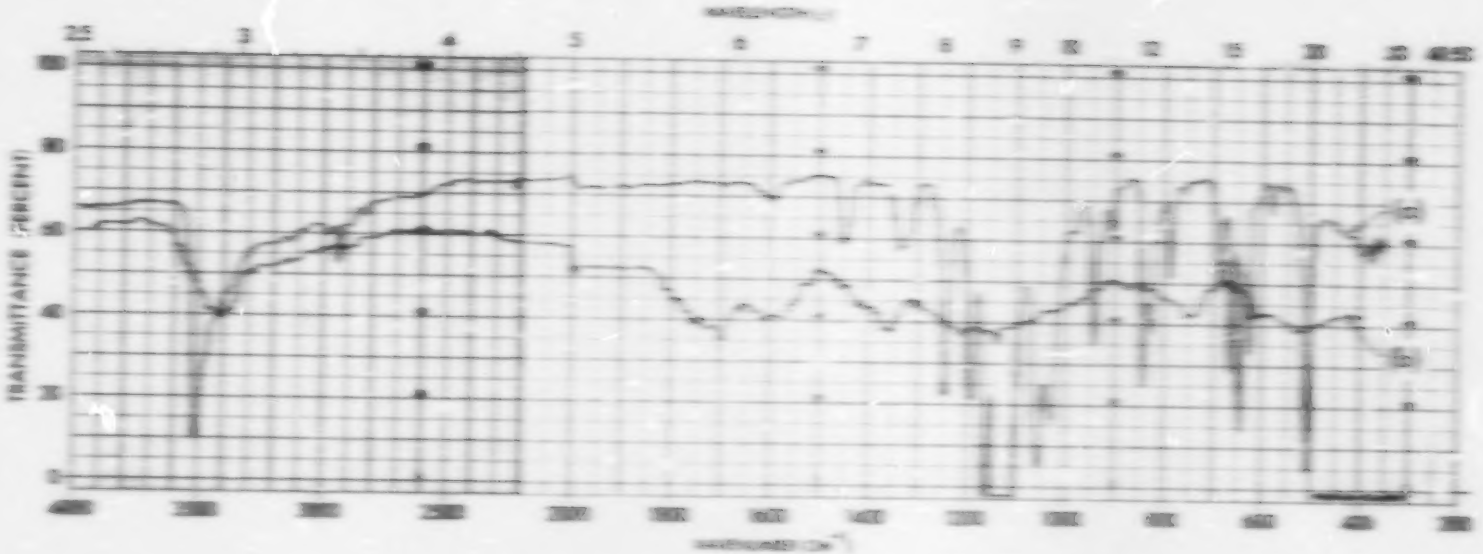


Figure 13. Infrared spectra of Kapton acetone extract (curve A) and its oxygen plasma reaction product (curve B)

atmospheric pressure to avoid continual depletion of solvent during the addition. Only the buret tip, inserted into the reactor above the plasma zone, was maintained at reduced pressure.

Feed techniques for solids are also under investigation. These include a two-tier reduced pressure forechamber in which the solids are placed. The solids will be fed into a kiln-type, angularly-positioned reactor which is rotated by means of a suitable, motorized transport.

7.3.3 Packed Bed Technology

Quartz Raschig rings were used in the reactor tube in order to increase the residence time of the feed materials in the plasma zone. Several variations in ring size and bed length were evaluated to determine maximum throughput under different packed bed conditions. Maximum throughput was defined as that quantity passing through the reactor which showed no methanol solvent in the mass spectrometer scans. Data are listed in Table 5. Without rings, decreased detoxification levels were observed because of excessively short, 0.1 sec, residence times.

On the basis of these runs, the application of packed bed technology can be considered for use where aqueous solution, pure liquids, and solvent systems are to be treated. Ring materials may be quartz or high-alumina ceramics which are not "lossy", i.e., do not show high dielectric loss factors, and thus do not "heat up" at 2450 MHz, which is the microwave frequency used in the process. In the batch detoxification of kepone solids, the packed bed approach was used successfully. For the continuous feed of solids and powders into beds of the above geometry, further investigation will be required for development of the technique.

7.3.4 Reduced Pressure Systems

Sargent-Welch 1397H Duo Seal mechanical vacuum pumps (approximately 400 liters/min pump capacity) were used for the development of the reduced pressure required for plasma formation. Liquid nitrogen, ice, or mixed ice-acetone traps were used, depending on the materials being studied, to trap out materials which would otherwise react with the oil or metal parts. This design has been adequate for the initial Phase I scale-up operation. However, it is likely that at the next level of scale-up more practical pump systems will be required, such as liquid ring seal or steam ejector pumps. These will obviate in large part the need for traps, which require filling, cleaning, etc., and can serve as a transfer medium for moving the acid gas products to a caustic scrubber for later disposal into municipal waste streams.

7.3.4 Analytical Processes

The methods used in this study have been described above. (See Section 5.3 and Appendix A.) The principal objective has been to determine the levels of detoxification/decomposition achieved in the expanded-scale plasma system, thereby evaluating the potential usefulness of

TABLE 5. INFLUENCE OF PACKED BED ON PMA-3%(PHENYLMERCURIC ACETATE) CONVERSION IN SERIES C PLASMA SYSTEM

Run No.	Packing of 45-mm Reactor: Ring Size o.d. x Length (mm)	Bed Length (cm)	Gas Flow (Standard liter/min)	Pressure (torr) Top	Pressure (torr) Bottom	Absorbed Power (kW)	Throughput (lb/hr)	Notes
31-88	6 x 6	16	8 to 16	120	-	4.7	2.35	First high-throughput run; reactor filled approximately one-half with rings
31-106	8 x 8	45	13.2	130	94	4.8	5.35	Reactor completely filled with rings
31-110	8 x 8	45	13.2	130	90	4.3	6.5	Repeat of 31-107
38-6	10 x 10	34	13.2	115	42	4.3	4.35	Largest rings of series
38-8	8 x 4	31	13.2 to 18.4	112	60	4.6	6.0	Rings fused near bottom part of power input
38-14	8 x 8	31	13.2 to 16.0	130	75	4.7	8.0 5.4	CH_3OH solvent observed at 8 lb/hr; disappeared when rate decreased to 5.4 lb/hr

the process. The methods adequately served this purpose. It will be necessary in further process developments, however, to refine the analytical techniques whereby in situ determination of ppm reaction products can be obtained. This will be required for analysis of gaseous as well as liquid (water, steam) effluents, before these streams can be disposed of into municipal sewage streams or directly to the air environment.

In line with these requirements, high-sensitivity gas chromatograph units with appropriate detectors are required for in-line determination of impurities, if such exist. Improvements in mass spectroscopy, and, later, installation of a gas chromatograph-mass spectrometer plus computer scan and readout of pesticides and toxic materials, can be a significant aid in assessing the completeness of the oxygen/steam plasma reactions, and thereby its usefulness as a detoxification method.

SECTION 8

CONCLUSIONS

1. The process of microwave plasma decomposition of organic materials has been applied successfully to the detoxification/destruction of hazardous organic wastes. A primary objective of the program - evaluation of the effectiveness of an expanded-scale plasma system - has been completed using hazardous organic compounds and wastes of current interest. The reaction products were identified in order to estimate their toxicity and to determine the potential for recycling/recovery of useful by-product materials.

2. This program has resulted in an expansion of the state of the art in microwave plasma detoxification from 1 to 5 g to 3 kg (7 lb) per hour. One hundred fifteen (115) runs were performed in the series. This scale-up has changed the perspective from one of academic interest to that of a realistic or practical level.

3. The commercial pesticides, Kepone, Malathion, phenylmercuric acetate, and methyl bromide; and the hazardous waste, polychlorinated biphenyl, can be detoxified beyond 99 percent in an oxygen plasma system. Malathion in pure liquid form was decomposed to > 99.999 percent and liquid PCB to at least 99.9 percent.

4. The potential for resource recovery has been clearly demonstrated for PMA-50, phenylmercuric acetate solution. The commercial form of this organomercurial was decomposed efficiently to yield metallic mercury, which is a salable item, plus oxides of carbon and water. The process may permit the additional recovery of valuable chemical feedstocks when applied to other organometallic pesticides or wastes which would otherwise be permanently lost.

5. The process itself is eminently safe. Microwave leakage is not detected near the applicator or the power supplies. Because reduced pressures (low vacuum) are used, the equipment, by its nature, does not permit materials loss through buildup of excess pressures and the consequent pressure blowoffs. Further, dangerous leaks will not occur, because the plasma unit would first shut itself down, and, simultaneously, terminate by means of interlocks, the introduction of feed materials. Process controls have not been complex in the initial scale-up development, but high sensitivity toxicity monitors at the ppm level will be required as the size of the equipment increases.

6. When compared with refractory incinerators, the microwave plasma systems have several advantages, such as potential for portability, or back-of-truck transport to a toxic materials' site, relatively low initial cost, leak-proof character, and, thus, the capacity for decomposing materials where no other techniques are satisfactory. For example, in an ordinary incinerator, the decomposition of phenylmercuric acetate, or any organomercurial waste, would result, unless all openings were totally closed, in an uncontrolled release into the environment of mercury metal or oxide particles. In the plasma system, the mercury is separated from the effluent gas stream and collected.

7. Since the plasma decomposition mechanism utilizes electronic energy, in which the applicator can be maintained barely hot to the touch, rather than thermal energy, materials-of-construction requirements are significantly less stringent. This results in lower materials costs, which reduces maintenance and repair expenses.

SECTION 9

RECOMMENDATIONS

This study, Phase I, Development of Microwave Plasma Detoxification Process, unquestionably points toward a phased, logical scale-up to a 20 lb/hr unit, and then to a 100 lb/hr version. A program, as outlined below, is recommended for the design, purchase, and construction of pilot-scale equipment and components. For development of the system, denoted as Phase II, specific engineering tasks are suggested.

- Materials Feed Operations. Techniques need to be developed and evaluated for the feeding of materials to be detoxified into the plasma reactor. These materials may be gases, liquids, solids, or slurries. The problem should be defined in detail, and the necessary equipment designed, installed, and tested in accordance with data obtained from the program recently completed.

- Microwave Power. Additional microwave power, above 5 kW at 2450, is suggested for the pilot process in order to expand capacity to the desired 20 lb/hr or more throughput. Power-generating components and ancillary equipment are purchasable off the shelf from microwave hardware suppliers.

- Microwave Plasma Applicator/Reactor. A new high-power applicator is needed for transfer of the increased microwave energy to the plasma reactor. The applicator is available as a custom-fabricated unit. The reactor materials suggested for use are catalog items.

- Product Receptor. For plasma reactions which involve in particular the formation of metals, cooling traps/heat exchangers should be designed and evaluated for product separation and condensation.

- Vacuum System. High-capacity liquid ring pumps should be evaluated for obtaining reduced pressures, based, in part, on their capability for acting as a medium for dissolving many of the acid products emitted from the reactor.

- Analytical Instrumentation. Process effluents should be analyzed for traces of potentially toxic impurities, if any of these materials are formed. Gas chromatographic units, infrared and ultraviolet spectrophotometers, and a quadrupole residual gas analyzer

(mass spectrometer) should be installed in-line for obtaining the required data.

It is also recommended that side-support studies be continued at the basic scientific level for evaluation of variables, such as microwave frequency and applicator/reactor technology to determine their potential effect on maximum size and throughput.

In conclusion, continued exploration of detoxification of "new" hazardous wastes should be maintained. In this regard, more than a hundred requests for information and data have been received during the last several months. These involved toxic waste and waste-related problems not previously considered for this application, thus indicating clearly the wide interest this new technology has engendered.

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Appendix A

MASS SPECTRA

A.1 EQUIPMENT

A quadrupole mass spectrometer Varian Model 974-0002 residual gas analyser was used to analyse the effluent gases from the reactor, as follows. A small quantity of gas leaving the plasma reactor is pumped past a variable-leak sampling valve which is located approximately 6 meters from the plasma exhaust. Figure A-1 is a schematic of the sampling valve interface with the plasma reactor and the residual gas analyzer. The sampling system consists of a quadrupole gas analyzer tube, a high-vacuum system for the analyzer tube, and a gas admittance system. A fraction of the plasma effluent gas is bled into the mass spectrometer, and is continually pumped through the sampling system by a second vacuum pump. Some of the gas is ionized by an electron beam ionizer in the analyzer section of the mass spectrometer. These gases not only form parent ions of the same mass as the neutral molecules, but also dissociate to form smaller ions. The ions are separated by mass by the quadrupole mass filter, and detected by an electron multiplier. The electron multiplier generates an electrical signal that is amplified and recorded. The filter is adjusted so that it passes ions of only one mass at a time. By controlling the filter, the distribution of ions is determined, yielding the mass spectrum of the gases present in the ionizer, up to a maximum of 250 mass units. Figures A-2 and A-3 are photographs of the residual gas analyzer hardware and electronics.

It should be noted, in a mass spectrometer system that is pumped to 10^{-10} atm, that there remain approximately 10^{9} molecules/cm^3. A sensitive mass spectrometer will register these background gases as background ions.

Vacuum pumps, particularly ion-getter or "Vac Ion" types, when used to maintain these low pressures, do not pump all gases with equal efficiency. Certain gases, e.g., argon, helium, etc., are pumped very slowly out of the mass spectrometer. This is the principal reason for the presence of one of the main residual background gases, argon, which produces the Ar^{+} ion, mass/charge M/E = 40, and the Ar^{++} ion, M/E = 20.

It should also be noted that, because of the dissimilar mass spectrometer response characteristics of the different gases within a mixture, quantitative comparisons using their relative peak heights are not reliable, and should not therefore be attempted.

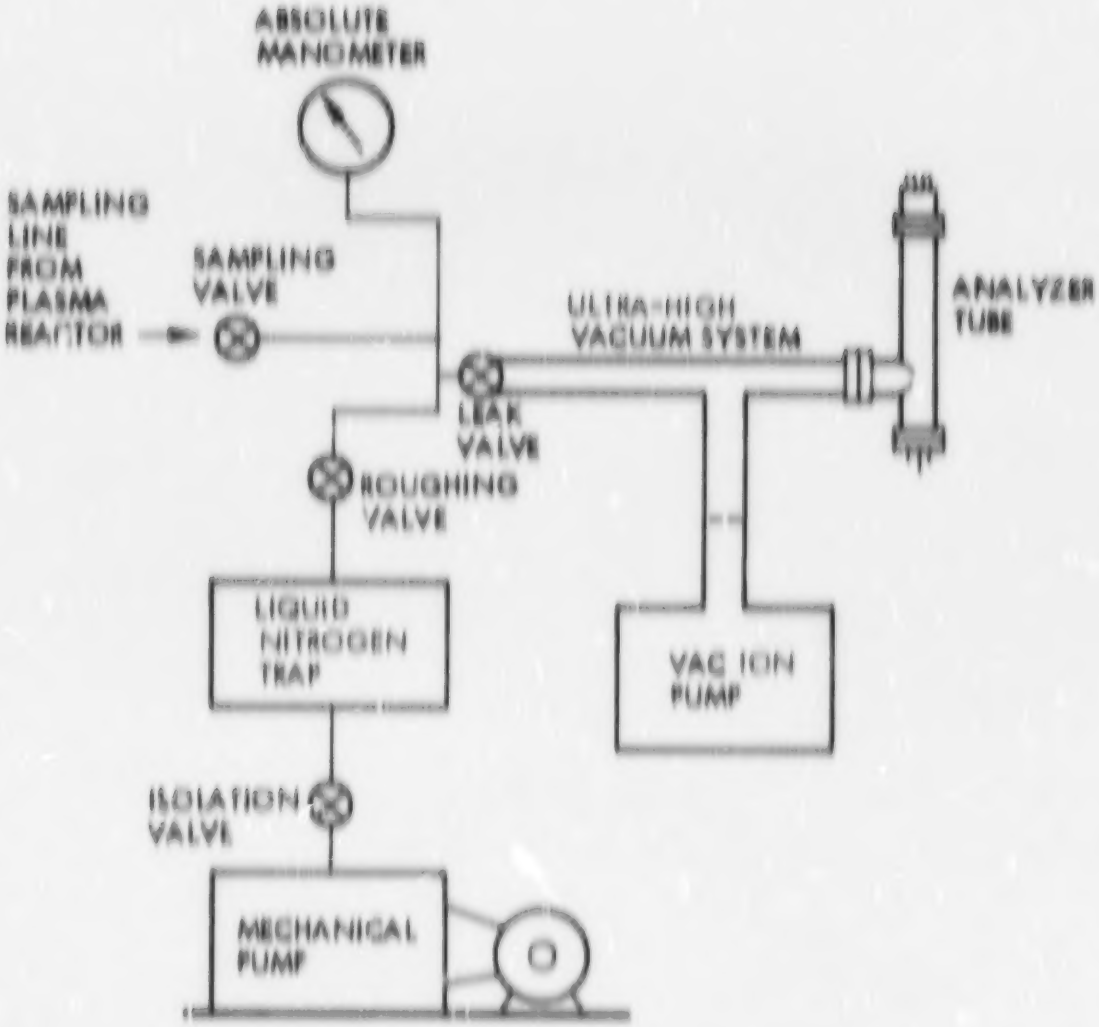


Figure A-1. Gas sampling system interface with plasma reactor and residual gas analyzer

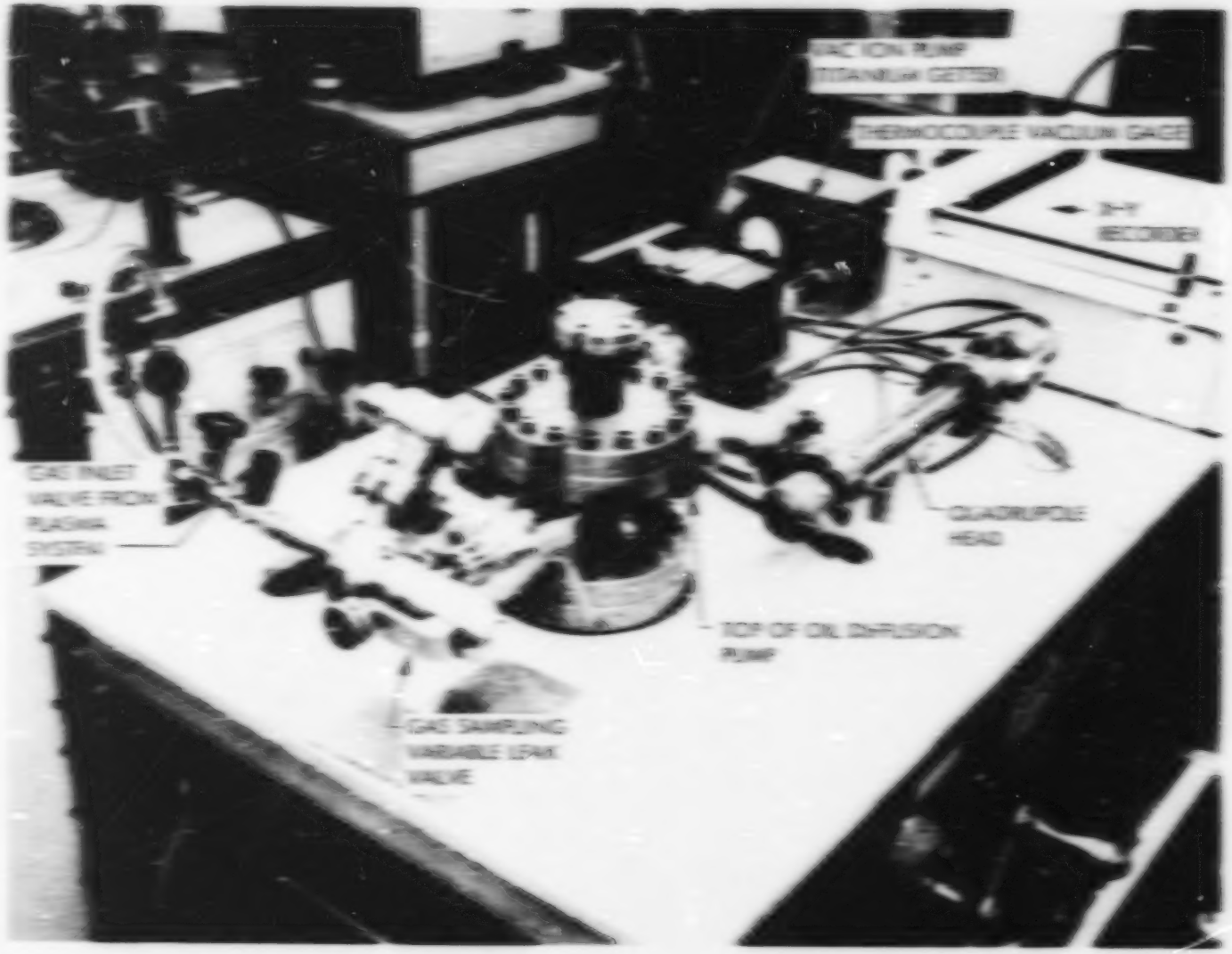


Figure A-2. Mass spectrometer residual gas analyzer – variable leak valve and quadrupole head

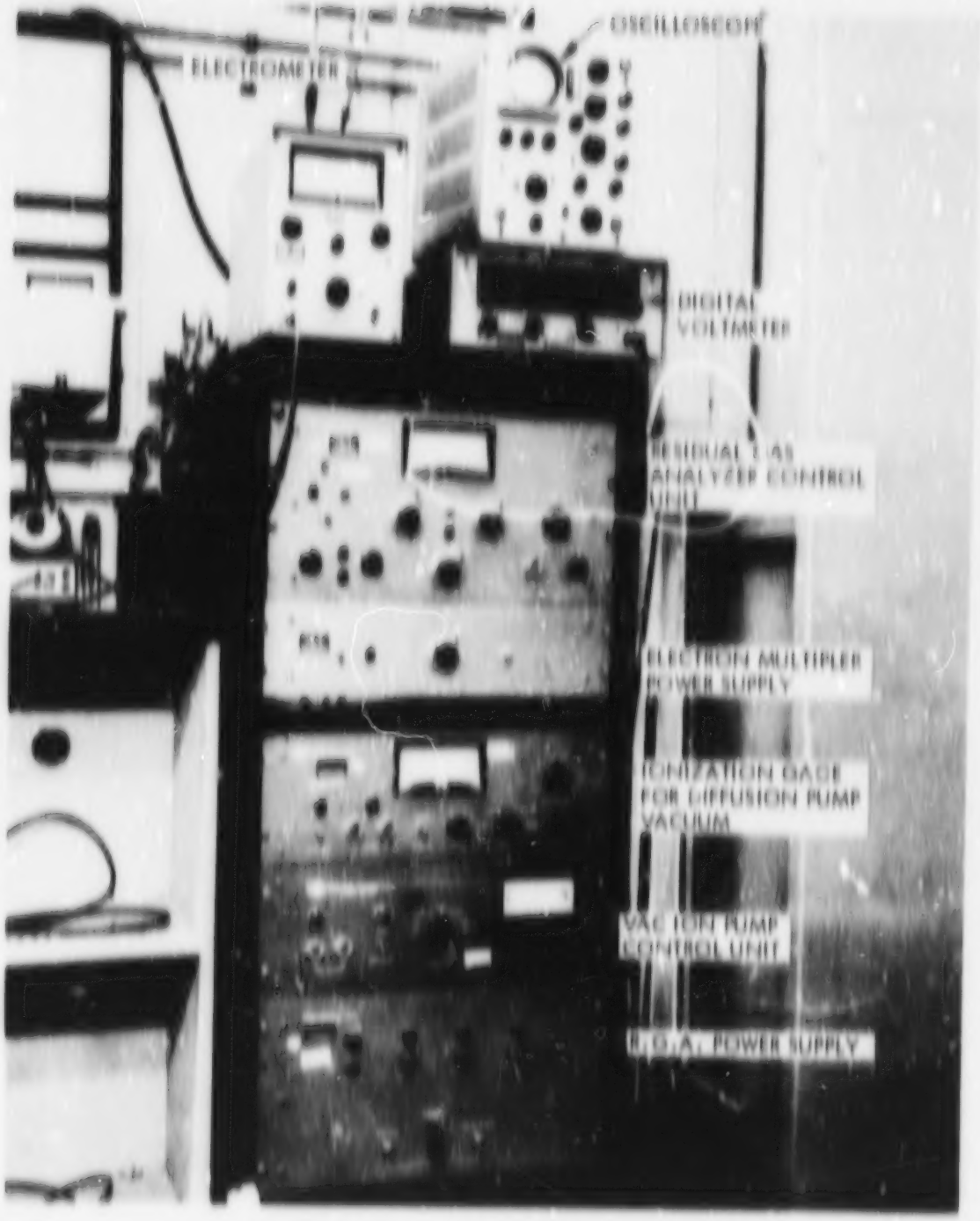


Figure A-3. Mass spectrometer residual gas analyzer – power supplies and vacuum gages

A.3 PESTICIDE AND HAZARDOUS WASTE SPECTRA

In the following spectra (Figures A-4 through A-10) are shown the masses of ions derived from the products of the respective oxygen and steam plasma reactions. These include scans from Malathion, PCB's, methyl bromide, phenylmercuric acetate, and Kepone. A brief commentary for each spectrum is included.

A.3.1 Malathion - Oxygen Plasma (Figure A-4)

The main gaseous products were carbon dioxide (M/E = 44, 28, 22, 16, 14, 12), carbon monoxide (M/E = 28, 16, 14, 12), water (M/E = 18, 17, 16), sulfur dioxide (M/E = 64, 48, 32), and, possibly, a small amount of acetylene (M/E = 26, 25). Most of the ions appearing in the oxygen plasma background were those formed from the residual background gases, such as argon (M/E = 40, 20), that are always present in the mass spectrometer.

A.3.2 Aroclor No. 1242 PCB - Oxygen Plasma (Figure A-5)

During the run, most of the oxygen was consumed. The main gases observed were carbon dioxide (M/E = 44, 28, 22, 16, 14, 12), carbon monoxide (M/E = 28, 16, 14, 12), and water (M/E = 18, 17, 16). Chlorine, Cl_2, (M/E = 70, 72, 74) was not observed, but gaseous hydrochloric acid (M/E = 35, 36, 37, 38) was detected. Most of the ions observed in the oxygen plasma background were those formed from residual background gases, such as argon (M/E = 40, 20), which are always present in the mass spectrometer.

A.3.3 Aroclor No. 1254 PCB - Oxygen Plasma (Figure A-8)

The main gases observed were carbon dioxide (M/E = 44, 28, 22, 16, 14, 12), carbon monoxide (M/E = 28, 16, 14, 12), and hydrochloric acid (M/E = 35, 36, 37, 38). Chlorine, Cl_2, (M/E = 70, 72, 74), was not observed. No appreciable amounts of water (M/E = 18, 17, 16) were observed; evidently, the hydrogen present in the $C_{12}H_5Cl_5$ molecules reacted to form hydrochloric acid HCl preferentially. There appeared to be excess oxygen (M/E = 32) present for these reactions. Most of the ions formed in the oxygen plasma background were those formed from residual background gases, such as argon (M/E = 40, 20), that are always present in the mass spectrometer.

A.3.4 Methyl Bromide - Oxygen Plasma, Laboratory-Scale Reactor, Quantitative Analysis (Figure A-7)

Quantitative analysis of the plasma compositions was performed by mass spectroscopy. In this method, the ratio of CH_3Br response (peak) heights were compared before and during the plasma reactions. Conventional analytical methods were precluded because of the toxicity of the methyl bromide gas. Figure A-7 illustrates the method. Decomposition was calculated as greater than 99 percent, which was the limit of sensitivity for the mass spectrometer unit.

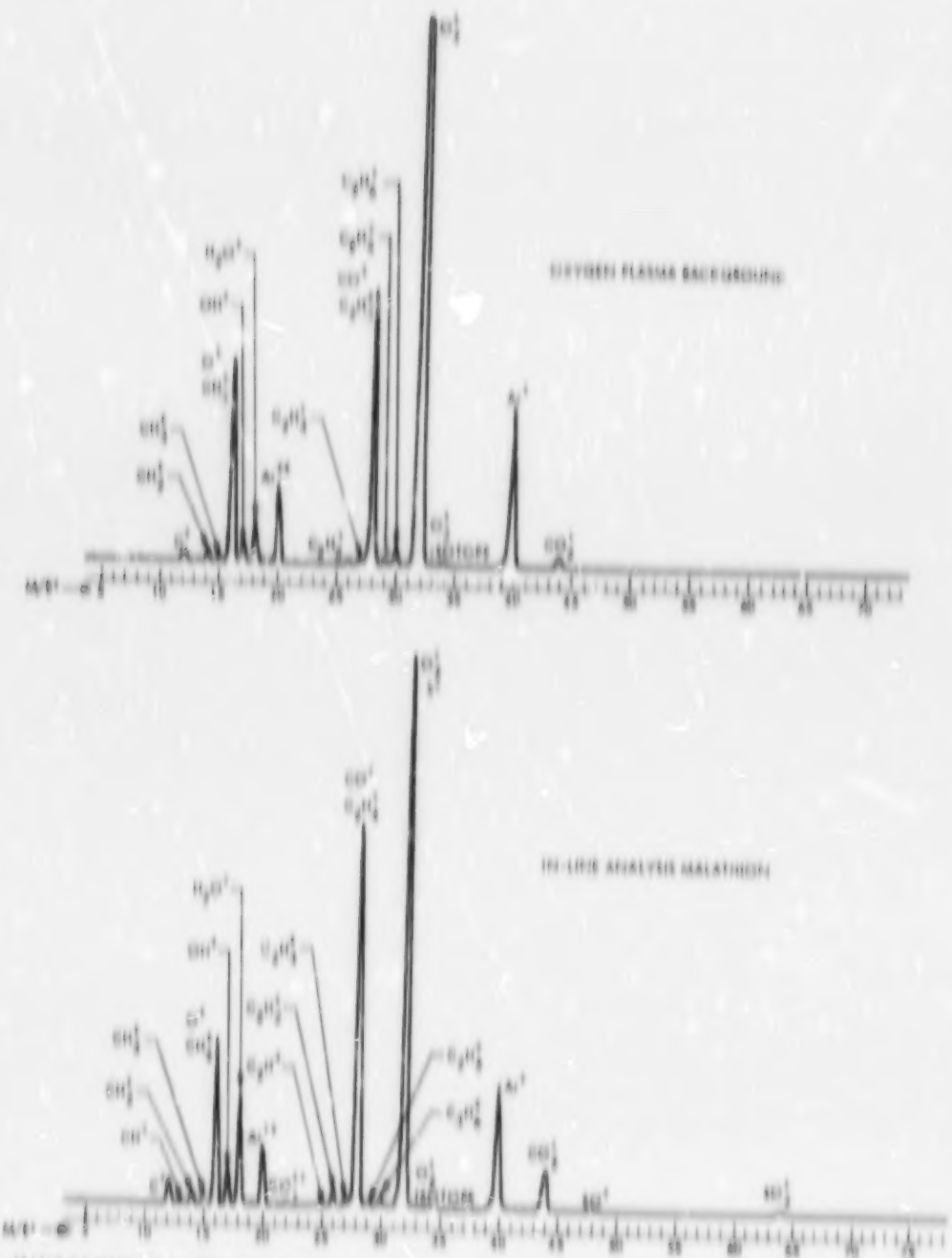


Figure A-4. Mass spectra of gaseous effluent from reaction of Malathion in oxygen plasma (Run 31-16)

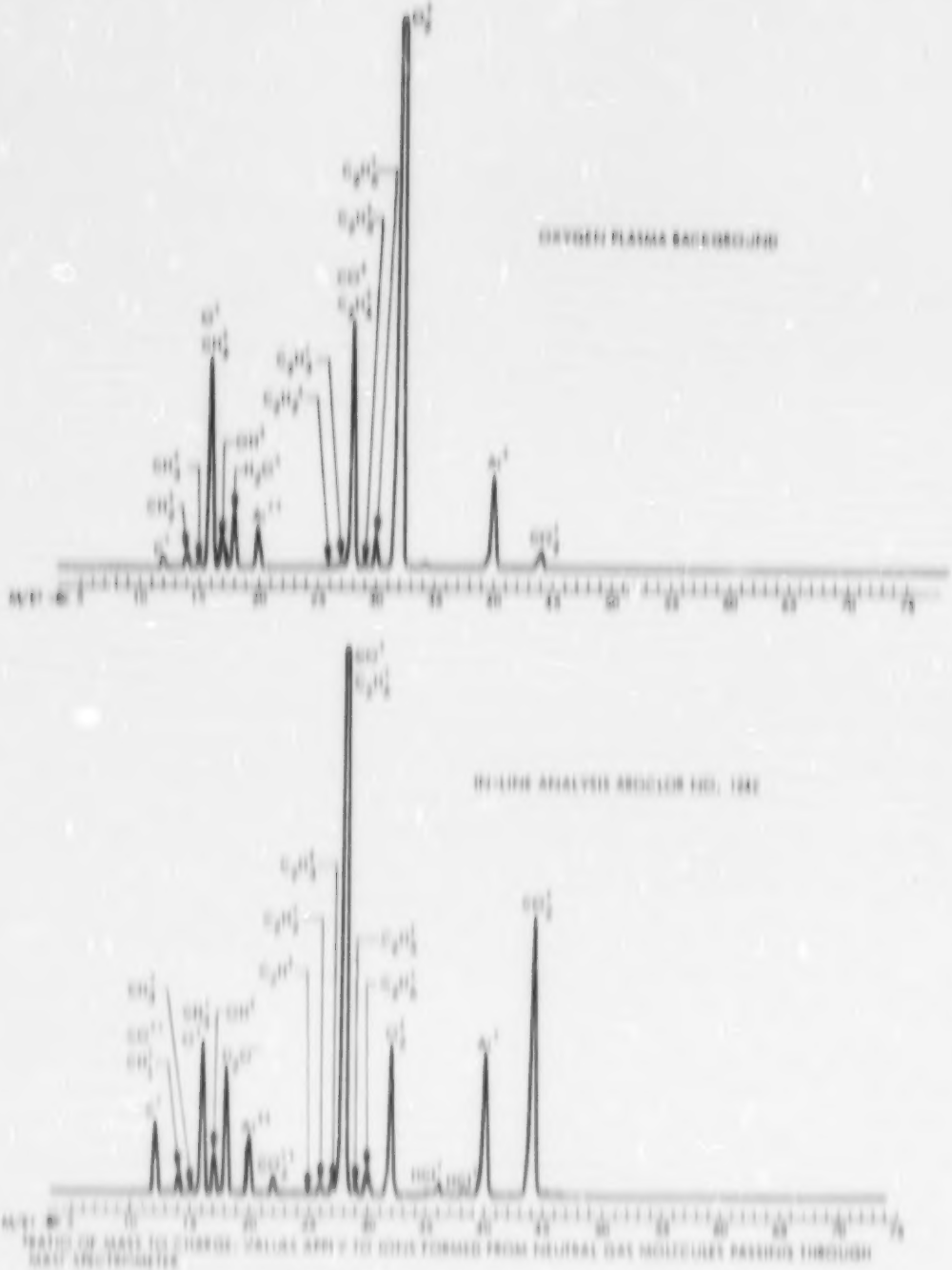


Figure A-5. Mass spectra of gaseous effluent from reaction of Aroclor No. 1242 PCB in oxygen plasma (Run 31-10)

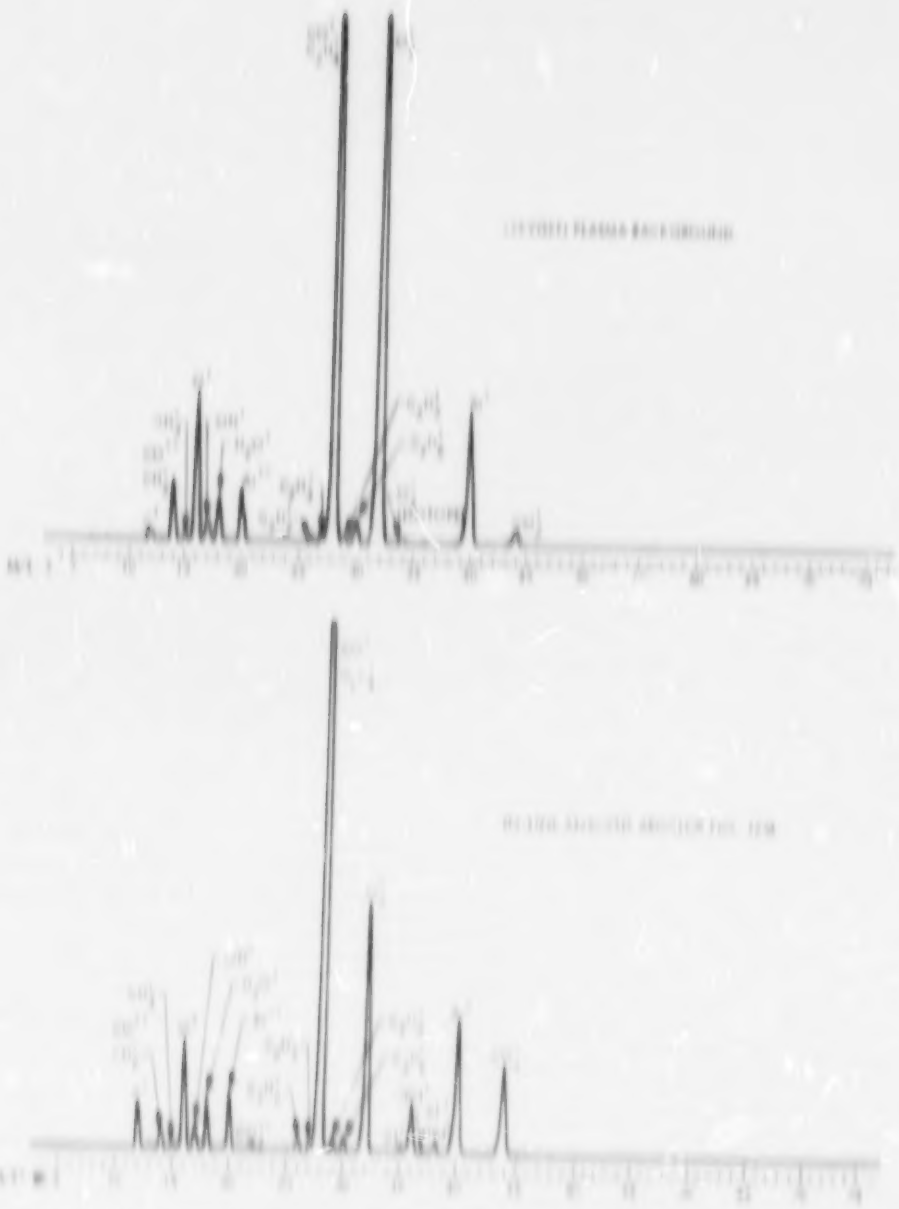
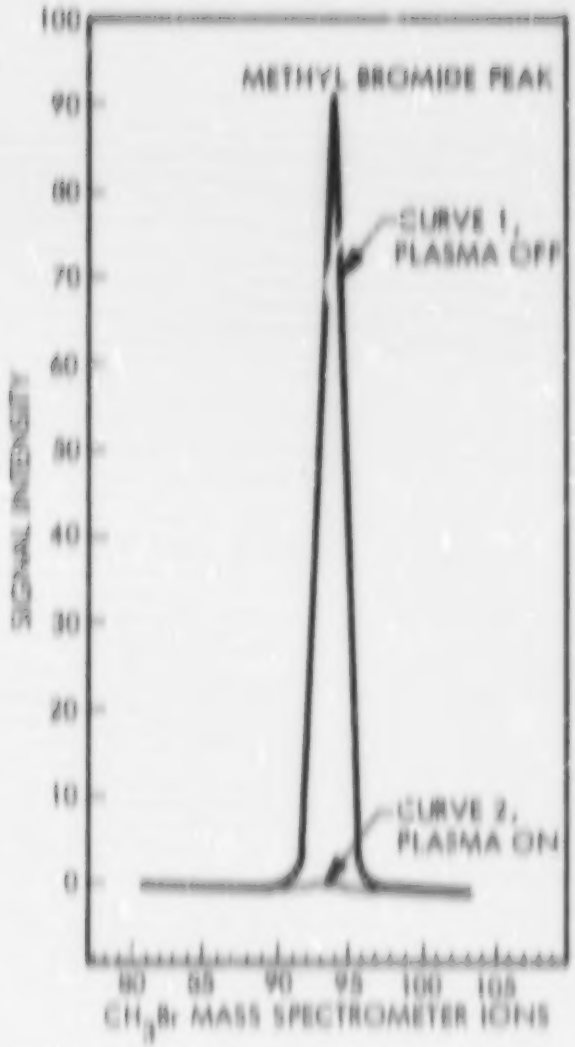


Figure A-8. Mass spectra of gaseous effluent from reaction of Aroclor No. 1254 PCB in oxygen plasma (Run 31-82)



Fraction of CH_3Br remaining when plasma on:

$$\frac{\text{Peak height plasma: On}}{\text{Peak height plasma: Off}} = \frac{0.5}{92} = \frac{1}{0.0054}$$

Therefore, CH_3Br decomposed >99% in plasma reaction

Figure A-7. Mass spectroscopic analysis of methyl bromide oxygen plasma reaction (Run 28-04)

A.3.5 Troysan PMA-30, Phenylmercuric Acetate – Oxygen Plasma (Figure A-8)

In-line analysis indicated that almost all the oxygen carrier gas (M/E = 32) had reacted. The main gaseous products were carbon dioxide (M/E = 44, 28, 22, 16, 14, 12), carbon monoxide (M/E = 28, 16, 14, 12), and water (M/E = 18, 17, 16) with minor amounts of low-molecular weight hydrocarbons. Most of the ions observed in the background plasma were those which are formed from residual background gases, such as argon (M/E = 40, 20), which are always present in the mass spectrometer.

A.3.6 Troysan PMA-30 – Steam Plasma (Figure A-9)

The main gases observed were carbon dioxide (M/E = 44, 28, 22, 16, 14, 12), carbon monoxide (M/E = 28, 16, 14, 12), water (M/E = 18, 17, 16), and a small amount of benzene (M/E = 78, 77, 50, 51, 52). There was no sign of the methyl alcohol solvent, which has a unique ion at M/E = 31. No sign of the possible product, dimethylmercury, was observed in which the high-mass range (not shown) was searched at high sensitivity. Most of the ions observed in the plasma background were those formed from residual background gases in the mass spectrometer, such as argon (M/E = 40, 20), or small amounts of aromatic ions (M/E = 78, 77, 76, 50, 51, 52).

A.3.7 Kepone – Oxygen Plasma (Figure A-10)

The main gaseous products observed were carbon dioxide (M/E = 44, 28, 22, 16, 14, 12), carbon monoxide (M/E = 28, 16, 14, 12), and water (M/E = 18, 17, 16). Further scanning in the high-mass spectrometer range, 1 to 250, using a high-sensitivity setting, showed no sign of phosgene or chlorinated hydrocarbons. Hydrogen chloride, extremely water-soluble, was found as an ice mass deposited in the liquid nitrogen trap.

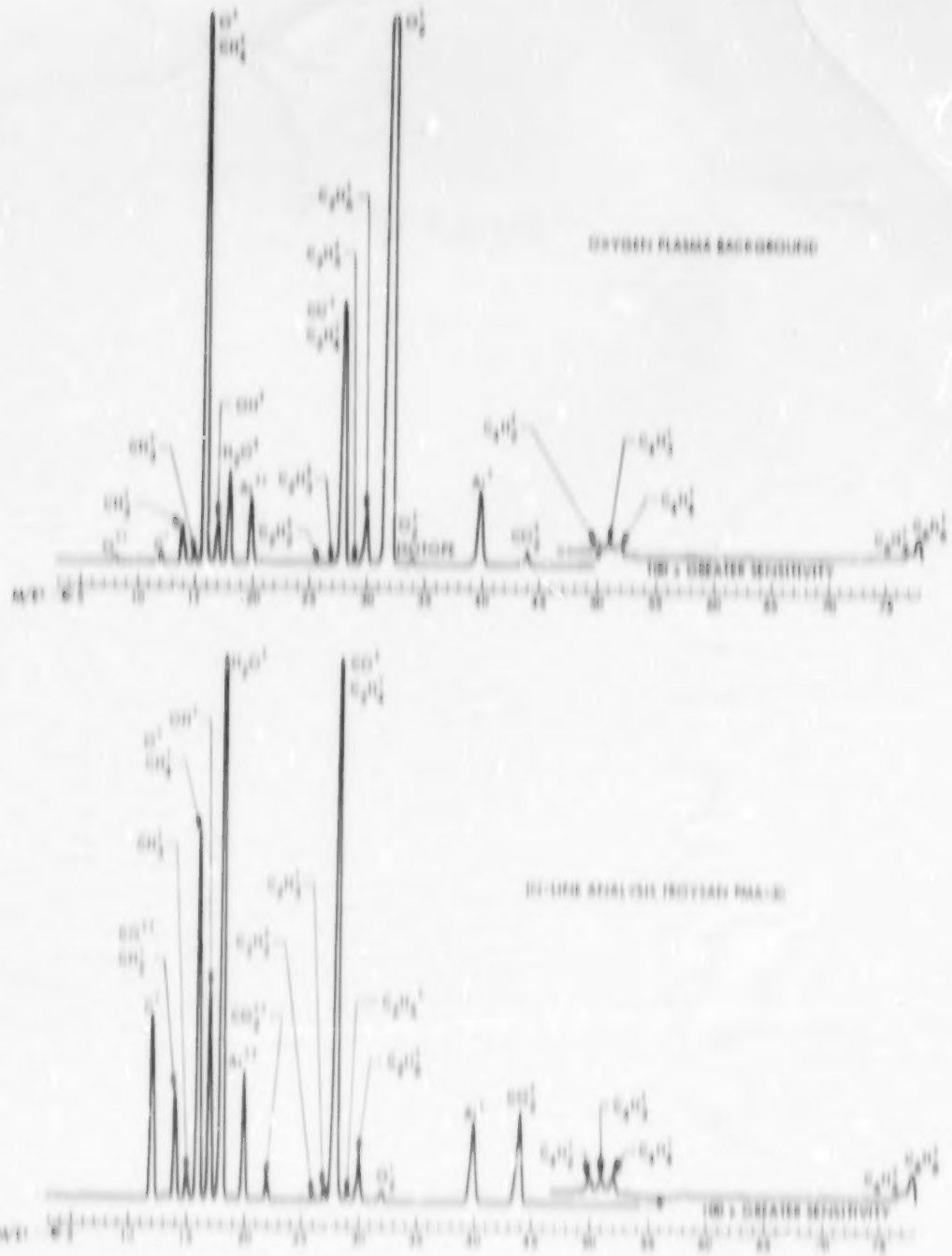


Figure A-8. Mass spectra of gaseous effluent from reaction of Troysan PMA-30 (phenylmercuric acetate methanol solution) in oxygen plasma (Run 31-118)

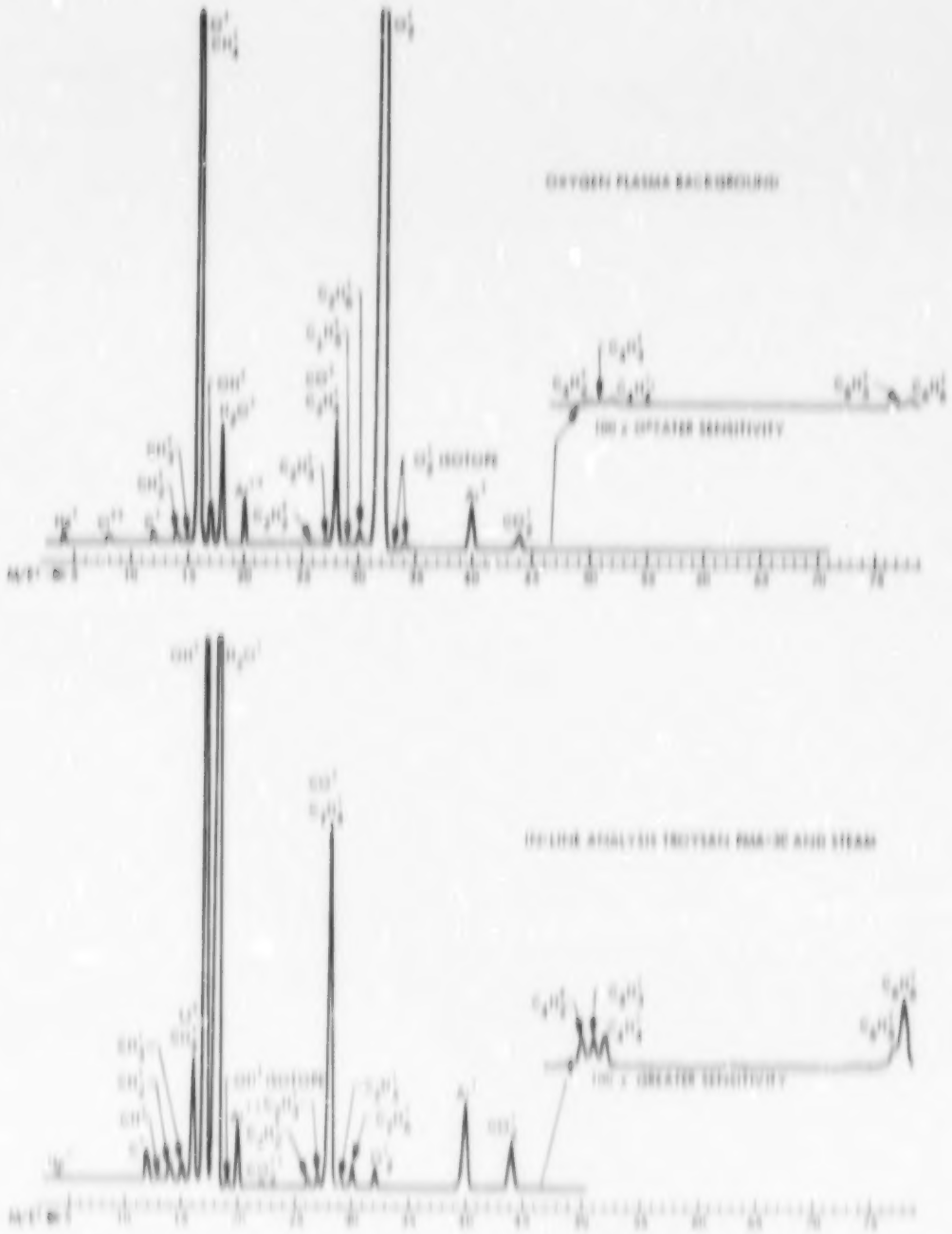
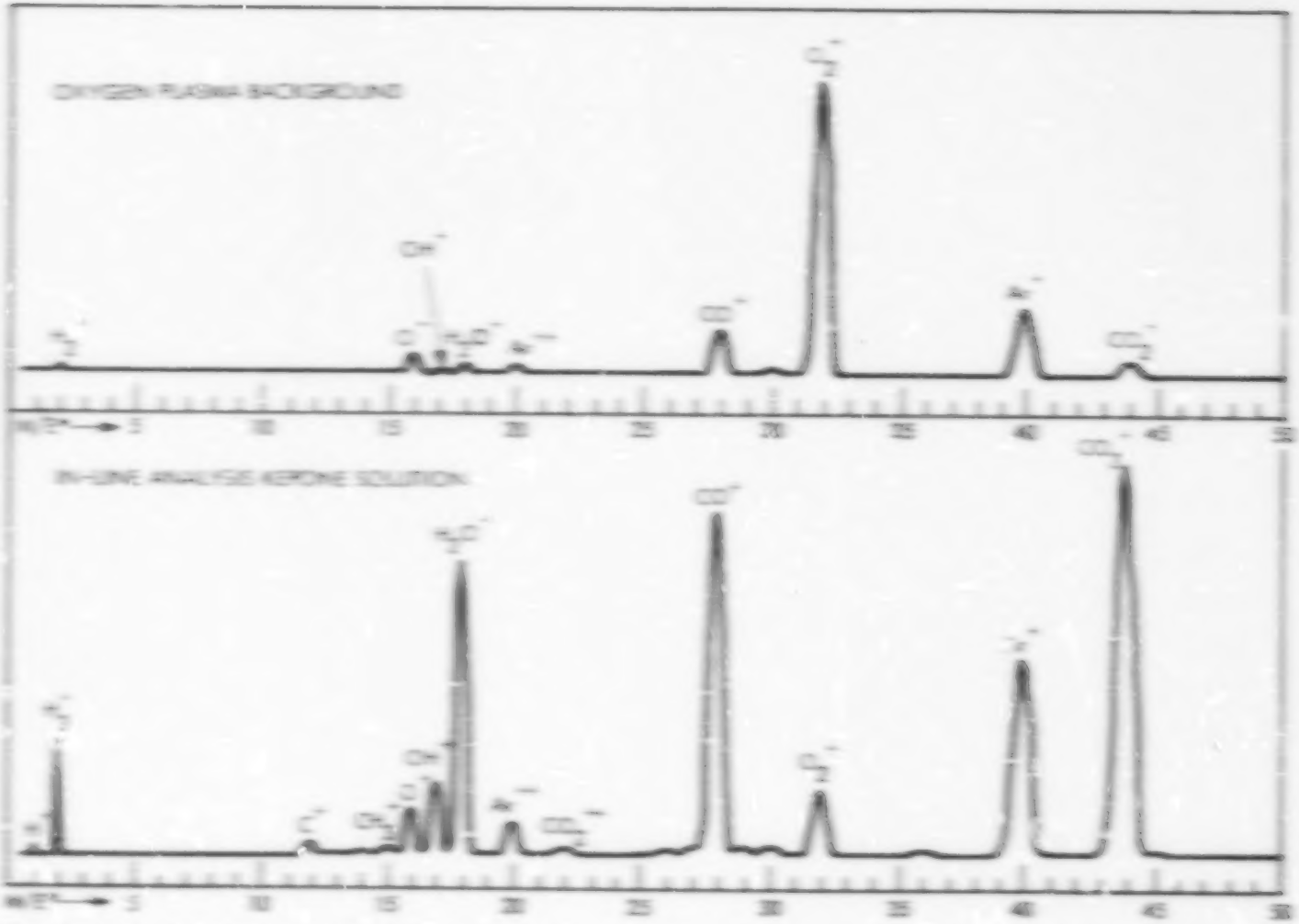


Figure A-8. Mass spectra of gaseous effluent from reaction of Troysan PMA-30 (phenylmercuric acetate methanol solution) in steam plasma (Run 31-190)



*RATIO OF MASS DIVIDED BY CHARGE VALUES APPLY TO IONS FORMED FROM NEUTRAL GAS MOLECULES PASSING THROUGH THE MASS SPECTROMETER.

Figure A-36. Mass spectra of gaseous effluent from reaction of kerosine-methanol/acetone in oxygen plasma

Appendix B

PROPERTIES OF PESTICIDES AND HAZARDOUS WASTES

Chemical and physical properties and specifications of the materials studied in the program are listed in this section.

B.1 MALATHION

American Cyanamid "Cythion" ULV (ultra low volume) grade was obtained from the manufacturer in commercial form, for which specifications are given as follows:

Chemical name:	O, O-dimethyl phosphorodithioate of diethyl mercaptosuccinate
Structural formula:	
Purity:	95%, minimum
Odor:	Slight, characteristic
Vapor pressure:	4×10^{-5} torr at 30°C
Boiling point:	156-57°C, 0.7 torr, slight decomposition
Melting point:	2.9°C
Solubility:	140 ppm in H_2O, 25°C. Soluble in most alcohols, esters, aromatic solvents, and ketones. Poor solubility in aliphatic hydrocarbons
Flash point, Tag Open Cup:	Greater than 163°C (325°F)
Viscosity:	40°C, 17 centipoises 25°C, 37 centipoises
Toxicity, LD_{50}, acute, oral:	1,375 mg/kg male albino rats, anticholinesterase behavior

B.2 POLYCHLORINATED BIPHENYLS

Two different grades were evaluated. These were Aroclor Nos. 1242 and 1254, obtained from Monsanto, St. Louis, Mo. Specifications and properties are listed below:

	Aroclor No. 1242	Aroclor No. 1254
Average molecular composition:	$C_{12}H_7Cl_3$ (60% between $C_{12}H_8Cl_2$ and $C_{12}H_5Cl_5$)	$C_{12}H_5Cl_5$ (60% between $C_{12}H_6Cl_4$ and $C_{12}H_3Cl_7$)
Chlorine (%)	42	54
Appearance:	Clear, mobile oil	Light-yellow viscous liquid
Distillation range (°C):	325-366	365-90
Flash point (°C), Cleveland Open Cup:	176-180	None to boiling point
Fire point (°C), Cleveland Open Cup:	None to boiling point	None to boiling point
Evaporation loss (%) 163°C (325°F), 5 hr:	3.0-3.6	1.1-1.3

B.3 METHYL BROMIDE GAS

Methyl bromide was obtained as a liquefied gas from Matheson Gas Products Company. Its specifications are as follows:

Chemical name:	Methyl bromide, or bromomethane
Formula:	CH_3Br
Purity:	99.5% CH_3Br (min.) 0.015% H_2O (max.)
Appearance:	Colorless
Odor:	None, except at high concentrations where it has a chloroform-like odor
Vapor pressure, 21°C&0°C):	13 psig (0.9 kg/cm^2 gage)
Boiling point, 1 atm:	3.5°C (38.2°F)

Freezing point, 1 atm:	-95.7°C (-138.7°F)
Flammability:	Limited to narrow range of 13.5-14.5% in air
Autoignition temperature:	538°C (998°F)
Toxicity:	Highly toxic; 20-ppm skin exposure, averaged, 8-hr day OSHA limits

B.4 PHENYLMERCURIC ACETATE, PMA

Commercial quantities of PMA solutions were obtained from Troy Chemical Company, and PMA 100 percent solids from Aldrich Chemical Company and American Drug and Chemical Company. Troysan PMA-30 was the principal material used for the detoxification studies. Specifications and properties are listed as follows:

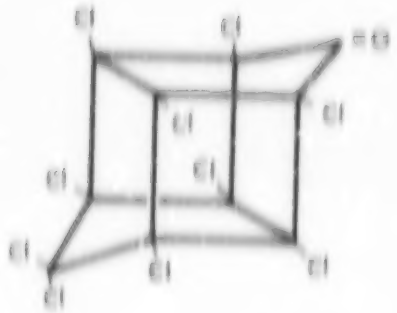
Chemical name:	Phenylmercuric acetate
Structural formula:	
Melting point:	149°C
PMA solids content in Troysan PMA-30:	30%, min.
Metal content in PMA-30:	18% Hg
Other components in PMA-30:	Principally methyl alcohol, ammonium acetate
Dilution in water PMA-30:	Complete
Toxicity, LD_{50}, acute, oral:	33 mg mercury/kg, rat test animals

B.5 KEPONE

Allied Chemical 89 percent Kepone concentrate, Code 9408, was used as the starting material. Approximately 0.5 lb was available for the tests. Properties are as follows:

Chemical name:	Decachloro-octahydro-1, 3, 4-metheno-2H-cyclobuta [c, d] pentalene-2-one, or chlordecone. (Ref. 12)

Structural formula:



Contents: 80% Kepone, 20% inert clay-type support

Melting point: Technical product, more than 90% pure; sublimes at near 350°C, with some decomposition

Solubility: Soluble in acetone, methanol (small amount exclusive of clay-support not soluble in C_6H_5OH). Isolatable as mono- or tri-hydrate; forms solvates with acids, alcohols, amines, and thiols, and soluble in strongly alkaline solutions. Recrystallizable from 90% aqueous ethanol

Toxicity, LD_{50}, acute, oral: 114 to 140 mg/kg, rat test animals

Appendix C

CHEMICAL REACTIONS IN ARGON AND HYDROGEN PLASMAS

This section includes the results of those plasma reactions which occurred in argon and hydrogen environments. The tests were continued during the program until it became apparent that these or related carrier gases would not be suitable for detoxification in a microwave plasma process.

C.1 MALATHION-ARGON AND MALATHION ARGON-OXYGEN PLASMAS

Decomposition reactions of Malathion in 800-850 W, 100 torr pressure, pure argon, and mixed argon-oxygen plasmas were investigated in the laboratory-scale plasma system. In pure argon, the yellow-brown products were offensive and malodorous, similar to mercaptan and disulfide compounds. In mixed 50/50 vol.% argon-oxygen, the products were essentially identical to that of the 100% oxygen plasma reactions, whereas in 80/20 argon-oxygen plasmas, mercaptan (skunk-like) but not sulfide, odors were again evident. Although analyses of these materials were not pursued actively, it was possible, nevertheless, to postulate the products of decomposition. This was based on the mass fragment formations which result from the ionization processes that occur during mass spectroscopic analysis of Malathion and related materials (13).

They are presented as follows:

5) H_2S and lower hydrocarbon sulfides, mercaptans

C.3 PCB – ARGON PLASMA REACTIONS

Aroclor No. 1242 liquid was passed through a 250 W argon plasma at 100 torr. In contrast to oxygen plasma results, a solvent-soluble, black tar-like oil formed in the reactor tube and dripped slowly down the sides during the reaction. The gases evolved were determined by mass spectroscopy to be the following:

(1)	Hydrogen chloride	HCl
(2)	Ethylene	$CH_2 = CH_2$
(3)	Acetylene	$HC \equiv CH$
(4)	Methyl chloride	CH_3Cl

Although the tars were not analysed extensively, later infrared determination of similar processes in hydrogen indicated that the black materials contained substantial quantities of unreacted PCB's.

C.3 PCB – ARGON-OXYGEN PLASMA REACTIONS

In a 50-50 volume percent oxygen/argon plasma, however, under laboratory-scale conditions similar to those described in subsection C.3, tar-like liquids, were not formed in the reactor. There were not more than traces, if any, of unsaturated hydrocarbons, chlorine oxide, carbonyl chloride, or methyl chloride in the gas effluent. The products were as follows:

(1)	Hydrogen chloride	HCl
(2)	Carbon dioxide	CO_2
(3)	Carbon monoxide	CO
(4)	Water	H_2O

C.4 PCB – HYDROGEN PLASMA REACTIONS

PCB's 1242 and 1254 were passed through the expanded-scale system in which a hydrogen plasma at 50 torr had been activated. Powers ranged from 4.0 to 4.6 kW. The principal gaseous reaction products, as determined by the mass spectrometer, were as follows:

(1)	Hydrogen chloride	HCl
(2)	Acetylene	$HC \equiv CH$
(3)	Methane	CH_4

A black, oily liquid with an aromatic naphthalenic odor dripped into the receiving tube after several minutes of reaction time. Analysis for chlorine content and infrared spectroscopy indicated that the liquid was principally a form of the original starting material.

C.5 METHYL BROMIDE – ARGON PLASMA REACTIONS

Gaseous methyl bromide (3 to 5 g/hr) was passed through 300 to 400 W argon plasmas at 50 torr in the laboratory-scale system. The products of reaction detected by the mass spectrometer were as follows:

(1)	Bromine	Br_2
(2)	Hydrogen bromide	HBr
(3)	Ethylene	$CH_2=CH_2$
(4)	Acetylene	$CH \equiv CH$
(5)	Methane	CH_4

Carbonaceous flake deposits were formed in the reactor tube. Quantitative analysis by the mass spectrometer showed that not less than 80 percent conversion had occurred.

C.6 METHYL BROMIDE – ARGON-OXYGEN PLASMA REACTIONS

Reactions of methyl bromide in 50-50 vol. % argon-oxygen plasmas yielded the following products as estimated by the mass spectrometer:

(1)	Bromine	Br_2
(2)	Hydrogen bromide	HBr
(3)	Ethane	C_2H_6
(4)	Carbon dioxide	CO_2
(5)	Carbon monoxide	CO
(6)	Water	H_2O

The unequivocal identification of several of these materials was difficult because of similarity in their masses, e.g., HBr^+, M/E = 80, 82, which registers adjacent to Br^+, M/E = 79, 81 on the spectrometer recorder charts. There was also no indication of the carbonaceous deposits, i.e., flakes, which were formed in the 100 percent argon plasmas. This is identical to the absence of carbon deposits reported above for 50-50 argon/oxygen PCB plasmas.